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TEMPERATURE DEPENDENCE OF PHOTO-ELASTIC CONSTANTS IN PLASTICS

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1. Introduction

High polymers generally exhibit a discontinuity in thermal expansion at a characteristic temperature. This temperature also marks a relatively abrupt change in other thermal, mechanical, electrical and optical properties. Ehrenfest[1] has termed these discontinuities as second order transitions. A considerable body of experimental data on high polymers has been reported by a number of investigators in this direction. Recently Subrahmanyam,[2] Krishnamurthi and Sivarama Sastry,[3] during their study of the variation of ultrasonic velocities with temperature in polymerized methyl methacrylate and polystyrene, have reported from this laboratory similar transitions. In the present investigation, these two polymers have been studied by photo-elastic methods.

2. Description of the Apparatus and Method of Observation

All the specimens needed were cut from cast sheets of polymethyl methacrylate or perspex and polystyrene. The cut surfaces of the samples were filed flat and smooth, and the samples were annealed at 90° C. for about 40 hours. The specimens were then worked out as plane parallel plates and were well polished. None of the specimens showed double refraction under crossed nicols in an unstrained condition.

A parallel beam of light from a sodium-vapour lamp was passed through a Nicol, the vibration direction of which was maintained at 45° to the vertical. The emergent beam then passed through the test-piece into a Babinet compensator, the principal axes of which were vertical and horizontal. After passing through the compensator the light was observed through an eyepiece containing a Nicol crossed with respect to the polarizer, and the usual Babinet fringes were obtained. When the specimen was compressed, the fringes shifted one way or the other and the magnitude of the shift was a measure of the path difference produced between the horizontally and vertically vibrating beams of light passing through the compressed specimen. Compression was produced by a lever arrangement.

Measurements of the fringe shift were made for stresses of about 100 kg./cm.^{2} in the case of perspex and 60 kg./cm.^{2} in the case of polystyrene. Following Pockels, the displacement of the fringes was measured at the middle of the length of the prisms at three places along its breadth, namely, near the left edge, the middle, and the right edge. The final measurements were made after ascertaining that the distribution of load was fairly uniform. The mean shift of the Babinet fringe in each case was obtained by taking the average of several readings. The path retardation read in terms of the head scale divisions of the Babinet compensator is a measure of the birefringence produced in the samples.

In order to study the variation of the induced birefringence with temperature, a compact electrical heater was built, the specimen being centrally situated within the enclosure. By means of a variac the voltage could be varied slowly and steadily till the requisite temperature was attained and a measurement on the Babinet was made only after ascertaining that the temperature was constant for about two hours. The procedure was repeated till consistent results were obtained at each temperature both while heating and cooling the specimens. Measurements of fringe shifts were made at intervals of 10° C., temperatures being read by a sensitive thermometer. The mean values of the Babinet shifts so obtained at each temperature were then made use of in deducing the relative stress-optical coefficients.

As the refractive index enters in the evaluation of the photoelastic constants, it is found necessary to determine the same for perspex and polystyrene at various temperatures. In the present investigation the usual method[4] in which dn/dt is directly measured as a function of temperature is employed. The method consists in cutting a plane parallel plate of thickness l out of the specimen and obtaining localized interference fringes by reflection from the two surfaces of the plate at normal incidence. The specimen was kept in a suitable furnace and the fringes, which consisted of sharp, bright and almost circular rings, were observed by means of a microscope. When heated, the fringes began to expand in both the cases and a continuous observation of noting the temperature corresponding to the passage of successive fringes was carried out. The rate of heating was so slow that it took eight hours to heat the specimen from room temperature to 90° C. The observations were repeated with cooling specimen, this also taking the same time.

The measurement of the expansion gives one the alteration in the path. Knowing Δt corresponding to each wavelength shift, dn/dt was calculated for the mean temperature making use of the formula

$$dn/dt = \tfrac{1}{2}l.\, dx/dt - n\alpha,$$

where α is the coefficient of thermal expansion at temperature t. The values of α at various temperatures were available from the work of Yasaku Wada.[5] The absolute values of indices of refraction (n_D) for sodium light at room temperature have been determined to three significant figures using the material in the form of tiny prisms, employing a spectrometer. In both the cases prisms having an angle roughly of about 60° were cut from sheets, 6·5 mm. in thickness, and the two sides of the prisms making the angle were well polished. Making use of these values of (n_D) at 25° C., the refractive indices at various temperatures were calculated from the data for dn/dt by numerical integration.

TABLE I

Values of n_D *at different temperatures*

Temperature ° C.	Perspex	Polystyrene
25	1·49300	1·59500
30	1·49047	1·59328
40	1·48542	1·58986
50	1·48043	1·58646
60	1·47539	1·58308
70	1·45906	1·57973
80	1·45193	1·54927
90	1·44447	1·54113

The calculated values of the refractive indices (n_D) at various temperatures for perspex and polystyrene are given in Table I.

3. Results and Discussion

The photo-elastic behaviour of isotropic substances is given by the equations:

$B_{11} - B = -q_{12}\cdot ZZ$; $B_{22} - B = -q_{12}\cdot ZZ$; $B_{33} - B = -q_{11}\cdot ZZ$; and $B_{23} = B_{31} = B_{12} = 0$.

In these equations $B = 1/n^2$, $B_{11}{}^2 = 1/n^2{}_{11}$, etc., where n is the refractive index of the undeformed specimen of an isotropic substance, n_{11}, etc., are the

components describing the Fresnel ellipsoid in the deformed condition, and ZZ, a simple linear compressional stress along the z-axis. q_{11} and q_{12} are the only two independent stress-optical coefficients, $(q_{11} - q_{12})$ being equal to q_{44}.

The determination of the relative stress-optical coefficients $(q_{11} - q_{12})$ was carried out by employing a Babinet compensator, the observations being given in detail in Tables II and III. 470·5 divisions of the Babinet compensator corresponded to a path retardation of one wave-length of sodium light.

TABLE II

Results for perspex

Temperature °C.	Mean shift in divisions of head-scale	$(q_{11} - q_{12}) \times 10^{13}$	$(p_{11} - p_{12}) \times 10^{4}$
27	104·0	2·626	1·133
40	110·0	2·846	..
51	116·0	3·031	..
61	121·0	3·271	..
71	130·0	3·572	..
80	139·0	3·922	..
91	150·0	4·321	..

TABLE III

Results for polystyrene

Temp. ° C.	Mean shift in divisions of head-scale	$(q_{11} - q_{12}) \times 10^{13}$	$(c_{11} - c_{12}) \times 10^{-10}$	$(p_{11} - p_{12}) \times 10^{4}$
32	144·0	4·733	2·782	1·371
42	137·0	4·540	2·722	1·236
52	130·0	4·347	2·672	1·161
62	122·0	4·115	2·614	1·075
72	113·0	3·903	2·552	0·996
81	100·0	3·678	..	..
92	84·0	3·157	..	..

From the mean shift of the Babinet fringe, the path differences corresponding to unit stress (1 dyne cm.$^{-2}$) and unit length (1 cm.) of light beam in the stressed specimen were calculated knowing that the path difference is $5{\cdot}893 \cdot 10^{-5}$ cm. for a shift of 470·5 divisions. The stress-optical constant in the corresponding direction of observation is $2\delta/n^3$. In the case of polystyrene the shift was in the same direction as for common glass while it was opposite in the case of perspex. Hence, the sign of $(q_{11} - q_{12})$ is negative for polystyrene and positive for perspex. Also an examination of Tables II and III reveals that the numerical value of the stress-optical constant $(q_{11} - q_{12})$ for perspex increases with increase of temperature while it decreases in the case of polystyrene. Furthermore the values of the stress-optical constant at the lowest temperature differ by 60 to 70 per cent. from those at about 90° C.

The values of the strain-optical constants $(p_{11} - p_{12})$ are calculated from the equation connecting p's, q's and the elastic constants, namely,

$$(p_{11} - p_{12}) = (c_{11} - c_{12}) \cdot (q_{11} - q_{12}).$$

The elasticity data on polystyrene at different temperatures have been obtained by Subrahmanyam.[2] The rigidity modulus of perspex is not available in the literature. Robinson, Ruggy and Elizabeth Slantz[6] have studied the stress-optical properties of polymethyl methacrylate as a function of temperature. However, their results do not give the complete data of the photo-elastic constants.

Temperature variation of the birefringence produced by stress in the above plastics is represented graphically in Fig. 1. A pronounced transition in the birefringence *vs.* temperature graphs of perspex and polystyrene will be noticed at 62° C. and 70° C. respectively. As has already been mentioned Subrahmanyam,[2] Krishnamurthi and Sastry[3] of this laboratory have studied the variation of ultrasonic velocities in perspex and polystyrene with temperature. They observed that both perspex and polystyrene show a transition at 61° C. and 70° C. respectively. The samples used by the authors and the above workers are taken from the same sheet of material. From the above facts it can be concluded that the present photo-elastic investigations in these two thermoplastics clearly show the existence of the transition points in good agreement with the earlier workers.

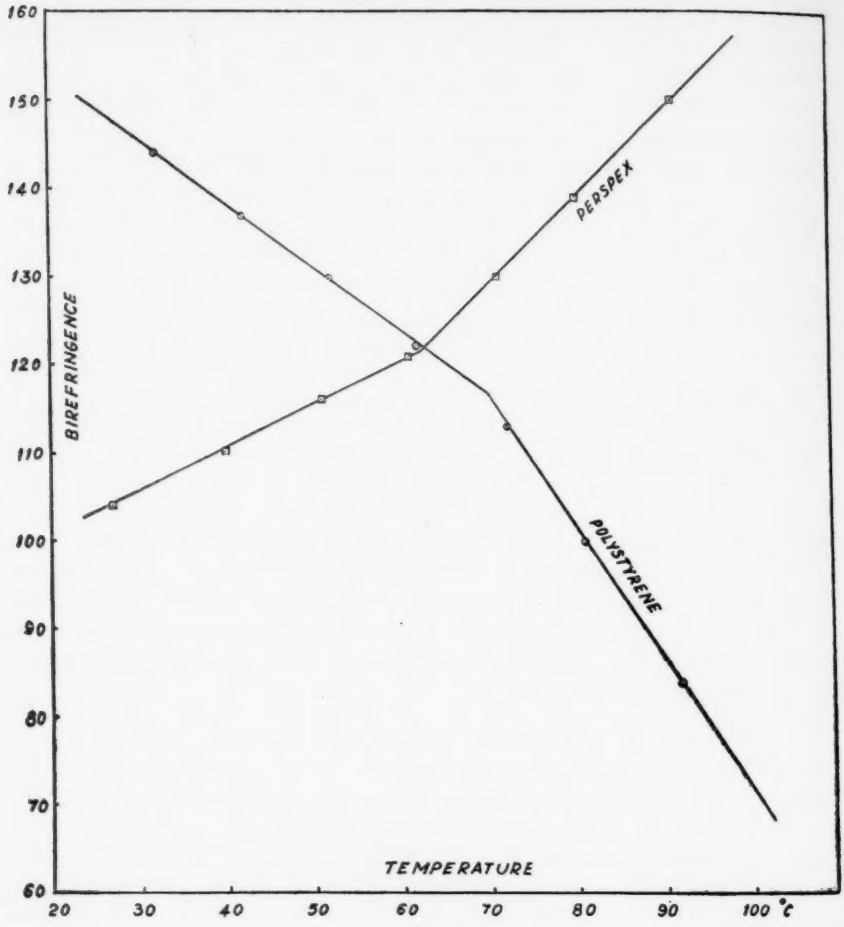

FIG. 1

4. SUMMARY

The birefringence produced in samples of polymethyl methacrylate and polystyrene when subjected to stress is measured at different temperatures employing a Babinet compensator. Graphs of birefringence against temperature are plotted for the temperature range 30 to 90° C. for perspex under 100 kg./cm.^{2} stress and for polystyrene under 60 kg./cm.^{2} The birefringence of the stressed methacrylate is positive and for polystyrene it is negative. The birefringence in the case of perspex increases with temperature

while in polystyrene it shows a decrease as the temperature increases. There is a transition point at 62° C. for perspex and at 70° C. for polystyrene. The relative stress-optic and strain-optic constants are evaluated at each temperature taking into consideration the temperature variation of the refractive index.

References

1. Ehrenfest, P. .. *Comm. Leiden, Suppl.*, 1933, **75 B.**
2. Subrahmanyam, S. V. .. *J. Chem. Phys.*, 1954, **22,** 1562.
3. Krishnamurthi, M. and Sivarama Sastry, G. *Nature*, 1954, **174,** 132.
4. Ramachandran, G. N. .. *Proc. Ind. Acad. Sci.*, 1947, **25 A,** 266.
5. Yasaku Wada .. *J. Phys. Soc. Jap.*, 1955, **24,** 287.
6. Robinson, H. A., Ruth Ruggy and Elizabeth Slantz *J. Appl. Phys.*, 1944, **15,** 343.

RAMAN SPECTRUM OF MAGNESITE

By D. Krishnamurti

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1. Introduction

According to Dana,[1] magnesite ($MgCO_3$) commonly occurs in massive and compact forms but clear single crystals are rare. It is not surprising therefore that few investigations have been made on its Raman spectrum. The only study reported in the literature was by Schæfer and others[2] who, using a single crystal, have reported a line at a frequency shift of 1096 cm.$^{-1}$ The opportunity for the present study arose due to the fact that some clear crystals from Brumadas, Bahia, Brazil were made available to us through the kindness of Dr. C. S. Pichamuthu. The density of a clear specimen was determined and found to be 3·02 gm./c.c., in fair agreement with the value 3·037 given in the *International Critical Tables*.

As the specimens were colourless, it was thought that the complete Raman spectrum could be readily recorded using the λ 2536·5 resonance line of mercury for excitation. Actually however, the crystals were found to be opaque to radiations of shorter wave-length than λ 2652. Hence the visible radiations of the mercury arc and a glass spectrograph had to be used, and the recording of the complete Raman spectrum was found to be far from easy, since in the first place the crystals were of rather small size and not completely free from flaws and since they also exhibited a faint luminescence. A strong and sharp line at a shift of 332 cm.$^{-1}$ and a strong but slightly diffuse line at 1096 cm.$^{-1}$ with a width of about ten wave-numbers were the principal features recorded on all the plates. By interposing a filter of $NaNO_2$ solution to suppress λ 4046 from the incident radiation and by placing a thin opaque strip just before the photographic plate to screen the exciting radiation λ 4358, clearer spectra were recorded in which could be observed and measured a line with a frequency shift of 212 cm.$^{-1}$ In some particularly clear spectrograms, a weak and rather diffuse line was found with a frequency shift of 735 cm.$^{-1}$ By analogy with the Raman effect in calcite one should expect one more line with a frequency shift in the vicinity of 1450 cm.$^{-1}$ A faint trace of such a line was found on one of the plates with an estimated frequency shift of 1460 cm.$^{-1}$

2. Discussion of Results

Magnesite has the same crystal structure as calcite belonging to the space-group D^6_{3d} of the trigonal system. Dolomite has also a similar structure, though it belongs to the space-group C^2_{2i}. In view of the similarity of crystal structure and chemical composition it is of interest to compare their Raman spectra. Table I shows the observed frequency shifts and their relative intensities in the case of calcite, dolomite and magnesite. The data for calcite are from a paper by Krishnan[3] while those for dolomite are due to Couture[4] by whom the Raman effect in dolomite has been investigated in detail.

Table I

Raman Frequencies

Substance	Frequency shifts in cm.$^{-1}$					
$CaCO_3$ ..	156 (8)	284 (15)		712 (2)	1086 (20)	1434 (5)
$CaMg(CO_3)_2$	176 (9)	301 (10)	335 (0·3)	724 (2)	1099 (23)	1444 (1·4)
$MgCO_3$ ..	212 (w)	332 (st)		735 (w)	1096 (st)	1460 (?)

As is to be expected, Table I exhibits a close similarity between the Raman spectra of calcite, dolomite and magnesite. All the frequencies of magnesite are definitely higher than those observed with calcite, this feature being more pronounced for the lattice oscillations than for the internal frequencies of the CO_3 group. An explanation of this feature is to be sought for in the fact that the lattice constants of calcite and magnesite are respectively 6·36 A.U., and 5·61 A.U., indicating a notable decrease in the interionic distances in the latter case. This would result in an increase of the interionic forces and hence also of the vibration frequencies involving the CO_3 groups.

Schæfer *et al.*[5] have studied the infra-red reflection and absorption spectra of magnesite and observed the following frequencies amongst others: Reflection Spectrum: 726, 889 and 1495 cm.$^{-1}$; Absorption Spectrum: 730, 877, 899 and 1430 cm.$^{-1}$ The only study on the far infra-red reflection spectrum of magnesite was by Coblentz[6] who observed a reflection maximum at 30·7 μ, *i.e.*, 326 cm.$^{-1}$ It will be noticed from the data that the frequency observed at 889 cm.$^{-1}$ in the infra-red does not appear in the Raman effect, whereas the frequency 1096 cm.$^{-1}$ observed in the Raman effect does not

appear in infra-red absorption. These facts are in accordance with the theoretical analysis of the vibrations of the calcite structure by Bhagavantam and Venkatarayudu.[7]

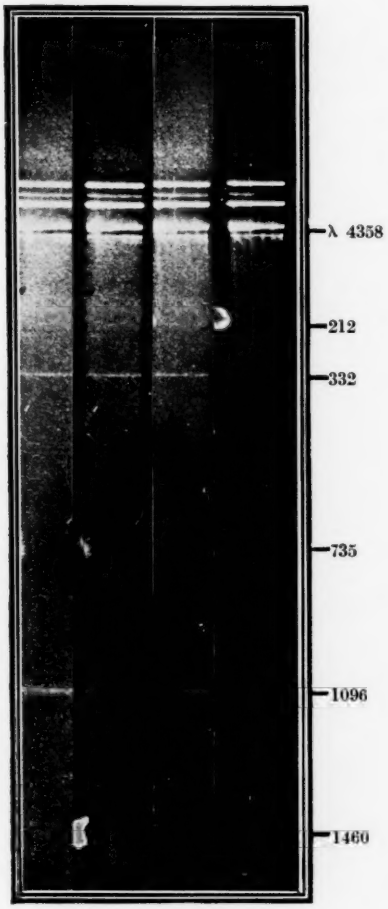
The author wishes to express his sincere thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for suggesting this investigation and for the kind interest he took in it.

SUMMARY

The Raman spectrum of magnesite ($MgCO_3$) has been investigated and found to be analogous in its features to that of calcite, as is to be expected in view of the similarity of structure. The frequency shifts observed are: 212 (*w*), 332 (*st*), 735 (*w*), 1096 (*st*) and 1460 (?) cm.$^{-1}$ All the frequencies and especially the two lowest are notably higher than for calcite and this is explicable as due to the smaller interionic distances and correspondingly larger force constants.

REFERENCES

1. Dana .. *Textbook of Mineralogy* (1932), John Wiley and Sons, New York.
2. Schæfer and others .. *Z. Physik*, 1930, **65**, 289.
3. Krishnan .. *Proc. Ind. Acad. Sci.*, 1945, **22 A**, 182.
4. Couture .. *Annales de Physique*, 1947, **2**, 5.
5. Schæfer and Matossi .. *Das Ultrarote Spektrum*, 1930, Verlag von Julius Springer, Berlin.
6. Coblentz .. *Supplementary Investigations of Infra-Red Spectra*, 1908, Carnegie Institution Publication, Washington.
7. Bhagavantam and Venkatarayudu .. *Proc. Ind. Acad. Sci.*, 1939, **9 A**, 224.



Raman Spectrum of Magnesite

STUDIES ON HEXACHLOROCERIC ACID

I. Isolation of Hexachloroceric Acid

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The reason for the marked instability of ceric halides have not been fully understood. Only the fluorides are known as normal salts of both cerous and ceric cerium.[1–3] Ceric chloride has not been isolated in the free state. When ceric hydroxide is dissolved in concentrated hydrochloric acid, a dark-red solution containing ceric chloride or the acid H_2CeCl_6 is obtained which rapidly decomposes with evolution of chlorine. The possibility of obtaining ceric chloride or hexachloroceric acid in absence of water was first reported by Koppel[4] and following his method, several double salts of the acid with organic bases have been prepared.[5–7] It is of interest to note that while the sulphato- and nitrato-ceric acids are stable in aqueous solutions, the chlorato-ceric acid is quite unstable. Although Koppel, for the first time, tried to isolate ceric chloride by carrying out the reaction between ceric oxide and hydrogen chloride in methyl alcohol, he only succeeded in preparing the pyridinium double salt of hexachloroceric acid. This paper deals with a systematic study for the isolation of hexachloroceric acid by using methyl alcohol and dioxane as reaction media to increase the stability of the products.

The reaction of hydrated ceric oxide and hydrogen chloride in methyl alcohol did not yield useful results in the isolation of hexachloroceric acid. The failure to isolate the reaction product from methyl alcohol solution could be either due to the high solubility of the product in methyl alcohol or due to the incapacity of the solvent to co-ordinate with the product as a solvate to yield a stable complex or due to both. Dioxane was next employed as the solvent. Dioxane was expected to be a good solvent to prepare ceric chloride since the solvent might increase the stability of the compound by forming a type of oxonium compound. Several inorganic halide dioxinates have been reported.[8–12]

It has been found in the present investigation that hexachloroceric acid crystallises out, under suitable conditions from a dioxane solution with four molecules of dioxane for every mole of the acid. The exact nature of the mechanism of reaction of hydrated ceric oxide and hydrogen chloride in dioxane and the formation of the crystalline product is not understood with

certainty. Although the formation of hexachloroceric acid is noticed when various other organic solvents are used as reaction media, *viz.*, methyl alcohol, ether, ethylene glycol mono methyl ether, etc., the crystalline product is obtained only in presence of dioxane. Evidence has been adduced to suggest that an anion complex of the type $CeCl_6$ is absent but that the product is a molecular compound of ceric chloride and hydrogen chloride of the formula $CeCl_4 . 2\,HCl$, co-ordinated with four molecules of dioxane. If the hexachloroceric acid and its pyridinium salt were complexes with cerium attached to the six chlorine atoms in a stable anion, silver nitrate solution (in non-aqueous medium) should give no precipitate. Again, if it is assumed that the anion consists of all the chlorine atoms combined with the cerium atom, there is no reason why one chlorine atom should behave differently in liberating iodine from potassium iodide. Studies on the physico-chemical properties like conductivity, molecular weight, vapour pressure and spectral characteristics—details of which are to be published in another part of the series—strongly support the view that the compound does not contain an anion complex of the type $CeCl_6$.--

EXPERIMENTAL

Materials used

(1) *Hydrated ceric oxide.*—Pure ceria was prepared from ceric ammonium nitrate by the iodate method. The ceric oxide thus obtained was converted into nitrate, dissolved in water and made alkaline with dilute ammonia. The precipitated hydroxide was oxidised with hydrogen peroxide and let stand for 12 hours. The yellow product was filtered, washed thoroughly with water, dioxane and petroleum ether when a free flowing yellow powder ($CeO_2 . 2\,H_2O$) was obtained.

(2) *Hydrogen chloride.*—Hydrogen chloride gas was prepared by the method of Harwood Tucker.[13]

(3) Methyl alcohol, dioxane and petroleum ether (30–75° C.) were purified and dried by standard methods.[14]

Analytical

(1) *Cerium.*—Cerium was precipitated as the oxalate, ignited and weighed as ceria.

(2) *Active chlorine.*—A known quantity of the material was put into acidified potassium iodide solution and the iodine liberated was estimated by standard sodium thiosulphate.

(3) *Total chlorine.*—A known weight of the substance was dissolved in 1 N sodium hydroxide solution and the contents acidified with chloride-free

nitric acid until the precipitated cerous hydroxide redissolved. The decomposition of the hypochlorite was effected by warming the solution with a little urea. The chloride content of the solution was estimated volumetrically by the silver nitrate method.

(1) *Reaction of hydrated ceric oxide and hydrogen chloride in methyl alcohol*

Hydrated ceric oxide (5 g.) and methyl alcohol (100 c.c.) were taken in a flask at 20° C. and hydrogen chloride was passed for nearly three hours with constant stirring, at the rate of about 6 litres per hour. The methyl alcohol solution turned orange-red in colour. The flask was kept at 2–3° C. for two days when the solution became more intensely coloured. The solution was filtered, out of contact with moisture and the residue on analysis was found to consist of 97·1% $CeO_2 \cdot 2\,H_2O$ and 3% $CeCl_3$. The filtrate was analysed for active chlorine and cerium contents. The estimation of total chloride was not attempted as it was not possible to free the solution completely of dissolved hydrogen chloride. It was noticed that for every gram atom of active chlorine, a corresponding quantity of cerium was present in the methyl alcohol solution. These results in general indicated that about 3% of ceric oxide was converted into ceric chloride or hexachloroceric acid which dissolved in alcohol producing the orange-red colour.

The above experiment was repeated at 0° C., − 15° C. and − 75° C. In the first two cases, there was not much difference in the rate of reaction and development of colour from the previous experiment. There was practically no reaction at − 75° C. The reaction could not be carried out for a long time as the methyl alcohol solution became very viscous, preventing the free passage of hydrogen chloride.

The product obtained by the reaction of 7·5 g. of ceric oxide and hydrogen chloride in 150 c.c. of methyl alcohol for three hours, was kept at 0° C. The progress of reaction was followed by estimating the active chlorine in aliquots of the solution every twelve hours. From these values, the amount of cerium (IV) in the solution was calculated. The results are presented in Table I.

These results show that in thirty-six hours, the ceruim (IV) content has increased nearly seven-fold, after which the rate of reaction is very slow.

Attempts at the isolation of hexachloroceric acid from methyl alcohol solution

About 100 c.c. of the ceric chloride in methyl alcohol, was subjected to vacuum desiccation when the intensity of colour and viscosity of the alcohol solution were found to increase. During the final stages an yellowish-red

solid separated which on further desiccation yielded only cerous chloride. Presence of free chlorine in the exit vapour was detected towards the final stages of evaporation. Concentration by cooling at 0° C. and at − 20° C. gave no better results.

TABLE I

Progress of reaction between ceric oxide and hydrogen chloride in methyl alcohol with time

Time (in hours)	% Ce (IV) in soln.
3	0·33
12	1·25
24	1·89
36	2·22
48	2·36
60	2·58
72	2·68

Removal of methyl alcohol from the solution was also attempted by passing a current of hydrogen chloride to maintain the acidity at a high value. The solid that separated was found to be merely cerous chloride. Separation of the ceric chloride by fractional freezing of the alcohol did not result in higher concentration of the ceric chloride. Fractional precipitation of the chloride by the addition of benzene, carbon tetrachloride, chloroform, ether, dioxane and petroleum ether did not yield any fruitful results. It can therefore be concluded that methyl alcohol is not a suitable medium for the preparation of hexachloroceric acid.

(2) *Reaction in presence of dioxane*

Hydrated ceric oxide (5 g.) suspended in dioxane (100 c.c.) was next treated with hydrogen chloride for nearly three hours. As there was considerable rise in temperature, the flask was cooled in water at 25° C. The development of the orange colour in the solution was much quicker than with methyl alcohol and left only a small quantity of residual solid. The flask was stoppered and left overnight at 2–3° C. when some orange-red,

needle-shaped crystals were formed. At the same time the colour of the solution had become paler. The solution was filtered through a sintered glass funnel, out of contact with moisture. The filtrate on analysis was found to contain cerium and active chlorine in the gram atom ratio of 1 : 1.

The residue in the funnel consisting of the crystalline mass and unreacted ceric oxide was dried in a current of dry air after washing with a small quantity of dioxane to remove the adsorbed solution and hydrogen chloride. The solid was then extracted with 50 c.c. of dioxane and filtered when a deep red filtrate was obtained, leaving a white residue on the filter. The white residue thus obtained was found on analysis to be a mixture of 87% ceric oxide and 13% $CeCl_3$. The deep red filtrate was then analysed for cerium, active chlorine and total chlorine and the ratio was found to be 1 : 0·994 : 6·10. From this, it was concluded that the crystals had the empirical formula H_2CeCl_6 with or without dioxane of crystallisation.

In subsequent experiments, 10 g. of ceric oxide were treated with hydrogen chloride, using the dioxane solution left as the filtrate, and the unreacted ceric oxide was removed by filtration. The filtrate separated into two layers, the heavier one being deep red and the lighter one orange-red in colour. On cooling the heavier layer to 2–3° C. for about 6 hours, a large crop of needle-shaped, bright, orange-coloured crystals separated, leaving behind pale orange coloured mother liquor. It was also noticed that the presence of hydrogen chloride was necessary for efficient crystallisation.

Analysis of the crystals

The crystals prepared as above were washed several times with petroleum ether and dried in a current of dry air, and analysed for cerium, active chlorine and total chlorine. The mean values of six different crops of crystals were: Ce = 19·48%; active chlorine = 4·94%; and total chlorine = 29 69%. Calculated percentage composition of $H_2CeCl_6 \cdot 4\ C_4H_8O_2$ is: Ce = 19·80%; active chlorine = 5·02% and total chlorine = 30·13%. The cerous chloride obtained by thermal decomposition of the crystals was also analysed. A known weight of the crystals was heated to 150° C., out of contact with moisture and cooled in a current of nitrogen and weighed. It was then analysed for cerium and chloride. The average value was 33·62% residue analysing to 56·18% Ce and 42·85% Cl. Calculated value of $CeCl_3$ from H_2CeCl_6, $4\ C_4H_8O_2$ is 34·87 % with 56·79% Ce and 43·21% Cl. These results conclusively show that the residue on decomposition of the acid crystals is cerous chloride, and the per cent. weight of $CeCl_3$ obtained agrees with the calculated value when the acid has the formula $H_2CeCl_6 \cdot 4\ C_4H_8O_2$. Because of the high reactivity of the crystals towards

light and moisture, experiments to estimate carbon and hydrogen did not give consistent results.

Preparation of salts

Koppel prepared the organic derivatives of hexachloroceric acid by treating the methyl alcohol solution with organic bases. The hexachloroceric acid crystals as prepared above, were also employed to prepare these compounds as follows. To a solution of the crystals in dioxane was added a solution of pyridinium chloride in methyl alcohol. Yellow shining crystals were thrown out, the amount of which increased by the addition of ether. The crystals were filtered off, washed with ether and analysed. The percentage composition was Ce = 26·80, active chlorine = 6·72, total chlorine = 39·26 and nitrogen = 5·12 agreeing well with the formula $(C_5H_5NH)_2\ CeCl_6$, for the complex.

With a view to prepare the sodium salt, the following methods were tried. Samples of methyl alcohol solution of the acid crystals were added to a methyl alcohol solution of sodium hydroxide, a solution of sodium methoxide in methyl alcohol and dry solid sodium chloride respectively. In the first two cases, there was immediate decolourisation with precipitation of cerous chloride. In the experiment where sodium chloride was added there was no immediate change, but on standing the solution got slowly decolourised, with deposition of white residue. Further studies on the preparation of salts of the acid are in progress.

Attempts to prepare the acid without dioxane of solvation

A portion of the heavy layer of liquid that is formed during the reaction of ceric oxide and hydrogen chloride in dioxane at 50° C. was subjected to evacuation at 25° C. and 0·1 mm. pressure. As the solid dried up, a pale yellow powder was left which was identified as cerous chloride. Repeated washing of the liquid with petroleum ether also resulted in getting cerous chloride as the residue. When the acid crystals were subjected to evacuation, decomposition took place leaving behind cerous chloride. Gentle heating of the crystals also resulted in decomposition. It was thus concluded that the acid got easily decomposed when the dioxane of solvation was removed.

SUMMARY

(1) The reaction of hydrated ceric oxide with hydrogen chloride in methyl alcohol under controlled conditions did not result in the isolation of hexachloroceric acid.

(2) Hexachloroceric acid has been obtained as a crystalline product from the reaction of hydrated ceric oxide and hydrogen chloride in dioxane.

(3) Conditions have been worked out for obtaining the crystals in a pure form. Analytical results agree with the formula H_2CeCl_6, 4 $C_4H_8O_2$. It has not been possible to obtain the acid without the dioxane of solvation.

(4) The pyridinium salt of the acid has been prepared, the analytical values agree with the formula $(C_5H_5NH)_2CeCl_6$ for the complex.

The authors' thanks are due to Prof. K. R. Krishnaswami for his keen interest and helpful suggestions during the course of the work. One of the authors (S. S. Moosath) is indebted to the University of Travancore for deputation to the Indian Institute of Science, Bangalore, to conduct this work.

References

1. Wartenberg, H. von .. *Z. anorg. allegem. Chem.*, 1940, **244**, 337.
2. Klemm, von W. and Henkel, P. *Z. anorg. Chem.*, 1934, **220**, 180.
3. Rimbach, E. and Kilian, F. C. *Annalen*, 1909, **368**, 101.
4. Koppel, J. .. *Z. anorg. Chem.*, 1898, **18**, 305.
5. Distefano, F. .. *Ann. Chim. applicata*, 1919, **12**, 130.
6. Caglioti, V. .. *Atti, II Congress, Naz, Chim. applicata*, 1926, 1182.
7. Grant, A. J. and James, C. *J. Amer. Chem. Soc.*, 1915, **37**, 2652.
8. Paterno, E. and Spallina, R. *Gazz. chim. ital.*, 1907, **37**, 106.
9. Kuran, W. J. and Wenzke, H. H. *J. Amer. Chem. Soc.*, 1935, **57**, 2162.
10. Kelley, C. J. and McCusker, P. A. *J. Chem. Soc.* 1943, **65**, 1307.
11. Rhienboldt, H. *et al.* .. *J. prakt. Chem.*, 1931, **129**, 278; 1937, **148**, 81; 1937, **149**, 30.
12. Brand, K. and Turck, I. *Pharm. Zentralhalle*, 1936, **77**, 591.
13. Harwood Tucker, S. .. *Chemistry and Industry*, 1949, 904.
14. Weissberger, A. and Proskauer, E. *Organic Solvents*, The Clarendon Press, Oxford, 1935.

STUDIES ON HEXACHLOROCERIC ACID

II. Reaction of Hydrated Ceric Oxide with Hydrogen Chloride Gas in Non-Aqueous Solvents

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Results of the reaction of hydrated ceric oxide and hydrogen chloride in methyl alcohol and dioxane have been detailed in Part I of the series. The reaction was studied in various liquids—both polar and non-polar—which are usually good solvents. Reaction was found to take place in some of the solvents, although in the absence of dioxane, no crystalline product could be isolated. The reaction is found to take place in such solvents which can form oxonium type of compounds with hydrogen chloride. The failure to isolate hexachloroceric acid from solutions in methyl alcohol, ether and ethylene glycol mono-methyl ether, in the absence of dioxane clearly shows that a suitable solvate is necessary for the complex formation in a crystalline form. Addition of dioxane to concentrated solutions in various solvents results in the formation of crystals having the composition H_2CeCl_6, $4\ C_4H_8O_2$. It appears that the solubility of the product is very much enhanced by the presence of OH group in the solvent as evident from the high solubility in methyl alcohol. The extremely rapid reaction in ethylene glycol mono-methyl ether and the non-separation of a second layer or crystals, support the view that the presence of tetravalent oxygen favours the reaction and that the presence of OH group in the solvent increases the solubility of the product formed. The separation of a second layer in ether shows the relatively low solubility of the product in ether which does not have the hydroxyl group. The exact nature of the mechanism of reaction in these solvents is not understood with certainty.

Experimental

Material used.—Hydrated ceric oxide and hydrogen chloride were prepared by the method detailed in Part I of the series. Dioxane, petroleum ether, benzene, chloroform, acetone, ether, ethylene glycol mono-methyl ether, formamide, and cyclohexanol were purified and dried by the standard methods.[1, 2]

Reaction in acetone, cyclohexonal, formamide, anisole benzene, and carbon tetrachloride:

(*a*) *Acetone.*—A mixture of hydrated ceric oxide (5 g.) and acetone (100 c.c.) was subjected to the action of hydrogen chloride for three hours. The acetone turned only light yellow in colour. When the flask was left at 2-3° C. for a day, the liquid became dark brown in colour with the formation of mesitylene oxide due to the polymerisation of acetone in presence of hydrogen chloride. Acetone was therefore considered unsuitable for the preparation of hexachloroceric acid.

(*b*) *Cyclohexanol.*—The previous experiment was repeated with cyclohexanol as the reaction medium. The ceric oxide remained unreacted. The solvent became slightly brownish in colour but no crystals separated on cooling the solution.

(*c*) *Formamide.*—When this solvent was used as the reaction medium, there was no change in the ceric oxide. The formamide became slightly brownish in colour but very little of the hydrochloroceric acid was produced.

(*d*) *Anisole.*—In this case also, the ceric oxide remained practically unreacted. But on keeping, the liquid became dark brown but no hydrochloroceric acid was produced.

(*e*) *Reaction in benzene and carbon tetrachloride.*—These solvents were tried as reaction media. As before, hydrated ceric oxide was suspended in these solvents and hydrogen chloride was passed. In both cases, there was no reaction and the ceric oxide remained unchanged.

1. *Reaction in ether.*—Hydrated ceric oxide (5 g.) and ether (150 c.c.) were taken in a flask and hydrogen chloride was passed at 10° C. for three hours, with stirring. The reaction was very slow, most of the gas being unabsorbed. Finally, the colour of the solution became orange. The flask was cooled at 2–3° C. The colour of the solution slowly became deeper and at the end of a week, about 5 c.c. of an oily red liquid got collected at the bottom. The ether layer had become red in colour. After another week, more of the red liquid had formed and then the contents of the flask were filtered. The residue on the filter was found to be mostly unreacted ceric oxide. The clear filtrate consisting of about 10 c.c. of the red oily lower layer and about 120 c.c. of the upper layer, was kept at 0° C. for several days. Crystallisation did not take place. All attempts to crystallise the substance were unsuccessful.

The two layers were separated and portions of each analysed for cerium and active chlorine. Both layers gave the atomic ratio of cerium to active

chlorine as 1 : 1. It was clear that small amounts of the hexachloroceric acid were formed in this solvent.

A portion of the lower layer was added to some dioxane. The two liquids mixed well on shaking. The solution was then kept at 2–3° C., when orange red, needle-shaped crystals separated out. The crystals were removed, washed with petroleum ether, dried and analysed. The composition of the crystals was found to agree with the formula H_2CeCl_6. $4\,C_4H_8O_2$. Hence it can be assumed that the red liquid that separated contained hexachloroceric acid, probably with ether of solvation.

2. *Reaction in ethylene glycol mono-methyl ether.*—When this solvent was used as the reaction medium in the above reaction, more vigorous reaction and quicker changes were noticed. Within about half an hour, nearly the whole of the ceric oxide dissolved and the solution became red and viscous. The temperature of the flask rose to about 60° C. The flask was disconnected from the hydrogen chloride system and the contents filtered. There was very little residue left on the filter and a clear, red viscous solution was obtained as the filtrate. Analysis showed that the gram atom ratio of cerium to active chlorine was 1 : 1.

Attempts were made to isolate a pure compound from this solution. Keeping the solution at 0° C. for several days did not effect crystallisation. Cooling to − 15° C. also did not make any change. Further cooling in solid carbon dioxide bath caused solidification of the entire solution without any separation of the acid. The solution was washed with petroleum ether. A larger number of washings with petroleum ether gave a pasty product. A pure product with a constant composition could not be obtained. Removal of solvent by evacuation was also not successful in getting the pure acid.

A portion of the solution was mixed with an equal volume of dioxane and kept at 2–3° C. Within a few hours needle-shaped orange coloured crystals appeared, which were removed, washed with petroleum ether, dried and analysed. The results indicated that the compound had the formula $H_2CeCl_6 \cdot 4\,C_4H_8O_2$. These facts clearly show that hexachloroceric acid is formed during the above reaction in presence of ethylene glycol mono-methyl ether but the solid acid could not be crystallised.

SUMMARY

(1) Benzene, carbon tetrachloride, formamide, cyclohexanol, anisole and acetone are not suitable media for the reaction of hydrated ceric oxide and hydrogen chloride.

(2) The reaction is found to take place to a limited extent in ether and nearly to completion in ethylene glycol mono-methyl ether forming hexachloroceric acid.

ACKNOWLEDGMENT

The author is thankful to Prof. K. R. Krishnaswami for his keen interest in the work.

REFERENCES

(1) A. Weissberger and E. Proskauer — *Organic Solvents*, The Clarendon Press, Oxford, 1935.

(2) A. I. Vogel .. *Practical Organic Chemistry*, London, 1951.

AN APPLICATION OF THE DIFFERENCE-PATTERSON METHOD

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(Communicated by Prof. G. N. Ramachandran, F.A.SC.)

1. Introduction

As early as 1942, Buerger (1942) has pointed out that the Difference-Patterson or the Difference-implication diagram could be used to find the positions of atoms in structure. Donnay and Buerger (1950) have computed the Difference-implication map to get the positions of Mg and Fe atoms in the structure of tourmaline. An extension of the Difference-Patterson (D-P) was applied by Frueh (1953) to facilitate the solution of order-disorder problems in minerals. Again, Buerger (1953) has suggested that an application of the minimum function method to the D-P maps could help in solving the crystal structure.

In a recent paper, Kartha and Ramachandran (1955) have shown that the D-P method can be systematically and successfully applied to analyse crystal structures. The present paper is mainly concerned with an attempt to apply the method to a more complicated example, namely, the isomorphous crystals di-*p*-tolyl telluride and di-*p*-tolyl selenide, whose structures have been worked out by Blackmore and Abrahams (1955 *a*, *b*). In their report, complete data are given of all the measured structure factors and these could be utilised to calculate the D-P diagram. The two compounds crystallise in the orthorhombic system, space group $P2_12_12_1$, with four molecules per unit cell. The unit cell dimensions are:

Selenide: $a = 25{\cdot}12$ Å; $b = 7{\cdot}99$ Å; $c = 5{\cdot}88$ Å.

Telluride: $a = 25{\cdot}33$ Å; $b = 8{\cdot}05$ Å; $c = 6{\cdot}01$ Å.

2. The D-P Diagram of the *b* Projection

The electron density projections given by them showed that the *b*-axis projection was free of overlap and so it was first tried. Using the data of $F(h0l)$, $|F(h0l)|^2$ were calculated for the two crystals and the Patterson function was computed in each case. The Patterson function of the selenide was subtracted from that of the telluride and the difference was plotted. The resulting D-P diagram is shown in Fig. 1.

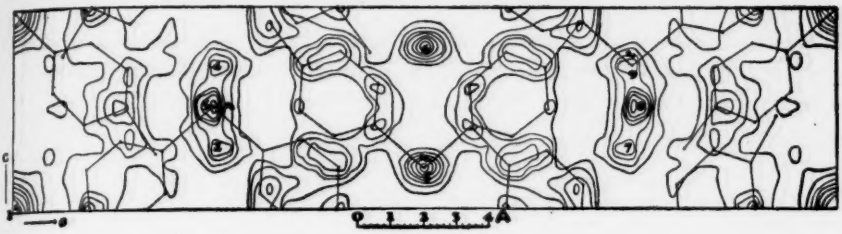

FIG. 1. The D–P projection of di-*p*-tolyl telluride and selenide along the *b*-axis. Contours for the heavy atom peaks are at intervals five times as much as the intervals of contours for other peaks.

The D-P diagram should contain only peaks at the termini of vectors joining the replaceable atoms (Te or Se) with themselves or the other atoms in the structure. The strong peaks, corresponding to the vectors joining the replaceable atoms only, occur in the diagram at the positions: (1) 0, 0; (2) 0·25, 0·30; (3) 0·25, 0·50; (4) 0·25, 0·70; (5) 0·50, 0·20; (6) 0·50, 0·80; (7) 0·75, 0·30; (8) 0·75, 0·50; (9) 0·75, 0·70. Of these, peaks 2, 4, 7 and 9 are of nearly the same strength while 3, 5, 6 and 8 are of double the strength, while peak 1 at the origin is four times as strong. The positions of the replaceable atoms could be obtained from the D-P diagram by translating it so as to make one of the peaks (*e.g.*, 2) coincide with the origin and marking out the positions of the peaks which superpose (the theory of this is simple). Since the structure has a centre of symmetry in the projection, this straightaway gives the positions of the replaceable atoms, namely 1, 3, 5 and 9. These are designated by a_1, a_2, a_3 and a_4 (Fig. 1).

In order to get the positions of the other atoms, the D-P diagram was then given a translation equal to $(a_2\, a_1)$, $(a_3\, a_1)$ and $(a_4\, a_1)$ so as to bring each of the other peaks in coincidence with the peak a_1 and the positions of the peaks which superpose were marked in each case. Owing to diffraction effects some of the fainter peaks were suppressed or displaced if they occurred near a strong peak in the D-P diagram. Consequently an average was taken of all the measurements. The molecule thus determined is shown associated with each of the replaceable atoms in Fig. 1.

In finding the superposition it must be remembered that in the D-P diagram a certain peak will be doubled or quadrupled, according to the replaceable atom peak with which it is associated. A certain amount of judgment is therefore needed in finding the superposed positions.

3. COMPARISON WITH EXACT STRUCTURE

The fractional co-ordinates of the atoms in the molecule with respect to the heavy atom are listed in Table I, together with the exact values for

TABLE I

Atoms	D–P method		Electron density method			
			Telluride		Selenide	
	x	z	x'	z'	x''	z''
C_1	−0·060	0·217	−0·0614	0·2161	−0·0604	0·1918
C_2	−0·056	0·408	−0·0545	0·4133	−0·0551	0·3972
C_3	−0·100	0·600	−0·0961	0·5602	−0·0994	0·5367
C_4	−0·148	0·500	−0·1458	0·5144	−0·1484	0·4700
C_5	−0·150	0·292	−0·1528	0·3160	−0·1539	0·2649
C_6	−0·100	0·175	−0·1108	0·1691	−0·1097	0·1262
C_7	−0·190	0·733	−0·1913	0·6733	−0·1955	0·6187
C_1'	+0·060	0·217	+0·0637	0·2128	+0·0602	0·2020
C_2'	+0·056	0·408	+0·0637	0·3960	+0·0558	0·4098
C_3'	+0·100	0·600	+0·1074	0·5428	+0·1002	0·5540
C_4'	+0·148	0·500	+0·1503	0·5016	+0·1481	0·4894
C_5'	+0·150	0·292	+0·1503	0·3201	+0·1516	0·2833
C_6'	+0·100	0·175	+0·1074	0·1732	+0·1077	0·1391
C_7'	+0·190	0·733	+0·1975	0·6583	+0·1957	0·6459

the telluride and selenide structures as determined by Blackmore and Abrahams (1955 *a*, *b*). It will be noticed that the agreement is fairly good except for the methyl carbon atoms C_7 and C_7' for which the z co-ordinates are appreciably different. This is due to the diffraction effect of the strong peaks. In all the eight positions, this particular atom is displaced roughly in the same way so that the displacement is not evened out by averaging.

Another point worthy of note is that the molecule as determined from the D-P diagram is symmetric about a line parallel to the *c*-axis. This symmetry is really absent, but in the superposition method of finding the peaks the differences noticed were not considered significant and an average was struck between the two halves of the molecule.

Further it must be mentioned that the Se and Te atoms are not exactly in the same positions in the two crystals. In fact a typical Te-Te vector has the components 0·26, 0·28 (as determined from the corresponding simple Patterson function) while the corresponding Se-Se vector is 0·26, 0·22 and in the D-P diagram the corresponding peak occurs at 0·25, 0·30 which is to be expected. So it is interesting to note that the D-P diagram has quite

sharp peaks corresponding to the replaceable atom interactions, in spite of the relative displacement of the corresponding atoms in the two isomorphous crystals and that the weaker peaks corresponding to the other interactions are also well defined. This shows that the D-P method can be confidently applied in general to isomorphous crystals even though the replaceable atoms may slightly differ in their positions.

4. Application of Vector Set Method to the Patterson Diagram

During the preparation of the Difference-Patterson diagram, it was observed that there was a close correspondence between the peaks in it and the peaks found in the ordinary Patterson diagram of the selenide and the telluride. This is to be expected because both Se and Te atoms are so much larger scatterers than the carbon atoms that the C-C interaction will be of small intensity compared to the Te- or Se-C and Te-Te or Se-Se interactions. Consequently the methods described in the previous section was applied directly to the Patterson projection of di-*p*-tolyl selenide along the *b*-axis. But for a background due to the C-C peaks which is seen from the fact that the minimum value of the Patterson function is nearly 2,000, as compared with value close to zero of the D-P map, this diagram is not inferior to the D-P diagram. However, there is the advantage that the shift and a small broadening of the peaks, which is present in the D-P diagram due to the difference in the positions of the atoms in the two crystals, is absent here.

Table II gives the co-ordinates of the atoms in one molecule obtained from it. The deviation Δ' from the exact value are shown in the table and may be compared with the deviations Δ found with the structure deduced from the D-P. It will be observed that the deviations are small and more or less the same but for the deviations in the position of the methyl carbon atoms, which are fairly large in both cases.

In order to test the usefulness of the method, the R value was calculated with the co-ordinates in Table II and was found to be 0·36 taking all the reflexions observed by Blackmore and Abrahams (1955 *b*) in this zone. It may be mentioned that taking the co-ordinates from the telluride structure unchanged the above authors found an R value of 0·45. Thus the simple Patterson could have been used directly to get an even better first approximation by the application of vector set method. In fact if it is assumed that the methyl carbon atom is in line with the two benzene ring carbon atoms, which are in the *para* positions relative to each other, then the mean deviation would be even less.

The same method was applied to the Patterson projection of di-*p*-tolyl selenide along the *c*-axis. The projection is shown in Fig. 2. As before

TABLE II

Atoms	D–P method		Electron Density		Image method		Deviation in Å Δ		Deviation in Å Δ'	
	x_1	z_1	x_2	z_2	x_3	z_3	$\Delta x=x_1-x_2$	$\Delta z=z_1-z_2$	$\Delta x'=x_3-x_2$	$\Delta z'=z_3-z_2$
Se	..	..	0·136	0·138	0·133	0·139	..	..	−0·075	0·006
C_1	0·073	0·356	0·075	0·330	0·071	0·339	−0·050	0·156	−0·100	0·054
C_2	0·077	0·547	0·081	0·535	0·065	0·572	−0·100	0·072	−0·375	0·222
C_3	0·033	0·719	0·037	0·675	0·033	0·656	−0·100	0·264	−0·100	−0·114
C_4	0·985	0·639	0·988	0·608	0·983	0·606	−0·075	0·186	−0·125	−0·012
C_5	0·983	0·431	0·982	0·403	0·973	0·42?	0·025	0·168	−0·225	0·014
C_6	0·330	0·314	0·026	0·264	0·025	0·289	0·175	0·300	−0·025	0·150
C_7	0·943	0·872	0·941	0·757	0·961	0·839	0·050	0·690	0·500	0·492
C_1'	0·193	0·356	0·196	0·340	0·195	0·339	−0·075	0·096	−0·025	−0·006
C_2'	0·189	0·547	0·192	0·548	0·201	0·572	−0·075	−0·006	0·225	0·144
C_3'	0·233	0·719	0·236	0·692	0·233	0·656	−0·075	0·162	−0·075	−0·156
C_4'	0·281	0·639	0·284	0·628	0·283	0·606	−0·075	0·066	−0·025	−0·132
C_5'	0·283	0·431	0·288	0·421	0·291	0·422	−0·125	0·060	0·075	0·006
C_6'	0·233	0·314	0·244	0·277	0·243	0·289	−0·275	0·222	−0·025	0·132
C_7'	0·323	0·872	0·332	0·784	0·305	0·839	−0·225	0·528	−0·675	0·330

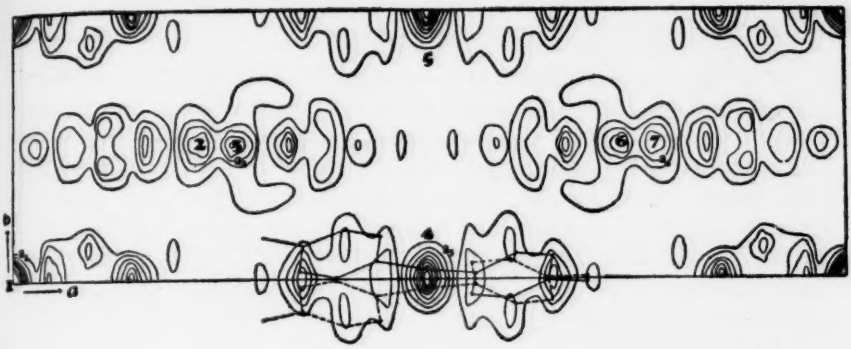

FIG. 2. The Patterson projection of di-*p*-tolyl selenide along the *c*-axis. Contour intervals are as in Fig. 1.

the strong peaks are designated by numbers from 1 to 7, and the positions of the replaceable atoms by a_1, a_2, a_3 and a_4. The y co-ordinate thus obtained is very close to 0·25. Because the y co-ordinate is close to $\frac{1}{4}$ every replaceable atom peak is doubled and further the rest of the molecule associated with the two peaks are related by a reflection on the *b*-plane. Hence it is difficult to uniquely interpret the diagram. The two possible positions of the molecule associated with one of the strong peaks are shown in figure. However if the presence of a benzene ring is previously known, a rough idea of the disposition of the molecule can be got. This projection is therefore more difficult to interpret than the previous one. It is thus seen that the interpretation of the heavy atom diagram or the D-P diagram may become difficult if the heavy atom or replaceable atom has special values for the parameters.

Thus, in general, it is clear that Buerger's idea of solving the Patterson map directly for the crystal structures can be profitably applied if there is a heavy atom and if there is no appreciable overlap in the projection. In the present case the structure had a centre of symmetry in the projection and no doubling of structure was introduced. If such a symmetry is not present, then the structure can be uniquely solved if (*a*) the number of replaceable atom peaks is greater than two, and (*b*) the group of replaceable atoms do not have a centre of symmetry (Kartha and Ramachandran, 1955).

The D-P technique is being systematically applied for solving unknown crystal structures in this laboratory.

In conclusion, the author wishes to express his sincere gratitude to Professor G. N. Ramachandran, for the keen interest he took in this study.

SUMMARY

The Difference-Patterson (D-P) technique is applied to a complicated example, namely, the isomorphous crystals, di-*p*-tolyl telluride and di-*p*-tolyl selenide, whose structures have been recently reported. It is shown that the D-P method can be confidently applied in general to isomorphous crystals, even though the replaceable atoms may slightly differ in their positions. Also, Buerger's vector set method is applied to the Patterson projections of the di-*p*-tolyl selenide along *b*- and *c*-axes. It is shown that Buerger's method can be profitably used when there is no appreciable overlap in the projection and if the heavy atoms or the replaceable atoms do not have special values for their parameters.

REFERENCES

1. Blackmore, W. R. and Abrahams, S. C. *Acta Cryst.*, 1955 *a*, **8**, 317.
2. ——— ——— .. *Ibid.*, 1955 *b*, **8**, 323.
3. Buerger, M. J. .. *Proc. Nat. Acad. Sci., Wash.*, 1942, **28**, 281.
4. ——— .. *Ibid.*, 1953, **39**, 674.
5. Donnay, G. and Buerger, M. J. *Acta Cryst.*, 1950, **3**, 379.
6. Frueh, A. J., Jr. .. *Ibid.*, 1953, **6**, 454.
7. Kartha, G. and Ramachandran, G. N. *Ibid.*, 1955, **8**, 195.

THE CONFIGURATION OF THE β-NAPHTHOL MALEIC ANHYDRIDE ADDUCTS

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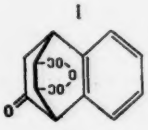
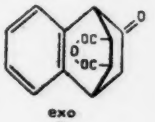
An adduct, formed from β-naphthol and maleic anhydride, by heating an equimolecular mixture at 220-40° C., was first isolated by Takeda and Kitabonoki.[1] By Clemmenson reduction of the adduct to a desoxy-compound, identical with the product of hydrogenation of the adduct of naphthalene and maleic anhydride, they showed that the structure of this adduct was represented by I.

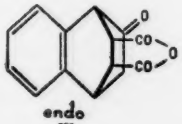
I



Later Takeda, Nagakura and Kitabonoki[2] isolated another adduct from the reaction product obtained by heating β-naphthol and maleic anhydride at 220-40° C. The steric configurations of these two adducts were then proposed on the basis of their dipole moments; the one with the smaller moment (2·86 D) being assigned the exo-configuration (II) and the one with the larger moment (6·54 D) the endo-configuration (III). They argued that in the exo-form the dipole moment of the carbonyl group (2·5 D) and the acid anhydride (4·32–4·05 D) will be in opposite directions while in the endo-form these two would be in the same direction.



exo
II



endo
III

The large difference in the two dipole moments and the good agreement between the two observed and calculated values makes the correctness of these assignments likely, but the misleading deductions possible from dipole moment

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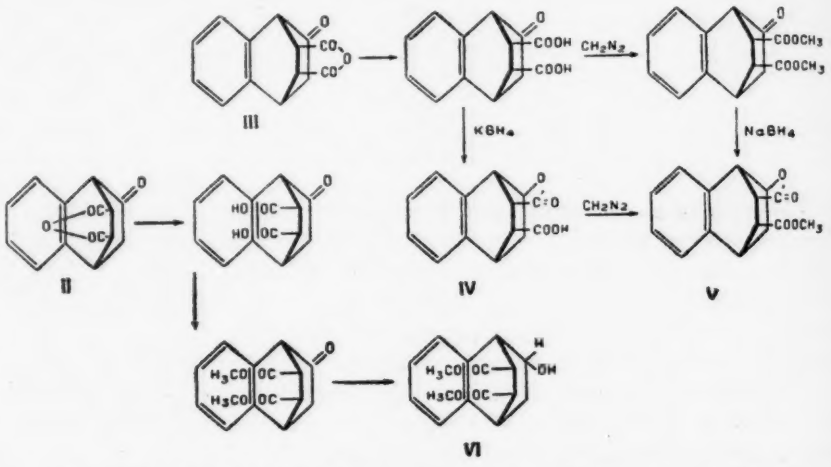
measurements in such ring systems [3, 4] makes a rigorous chemical proof desirable. This has now been provided by the following transformations. The two anhydrides were converted into the acids by boiling with water and then into the respective esters by diazomethane. These isomeric keto esters were then reduced by sodium borohydride in methanol. The endo-form gave a lactone ester $C_{15}H_{14}O_4$ (V) by elimination of methanol, while the exo-form gave the normal reduction product $C_{16}H_{18}O_5$ (VI). The endo acid obtained by boiling the endo adduct with water was also reduced with potassium borohydride in aqueous medium and the resulting lactone acid (IV) converted into its ester by diazomethane. It was found that this ester was identical with the lactone ester obtained by the reduction of the dimethyl ester of the endo acid. The scheme is given below.



The peak in the infra-red spectrum of the lactone ester (Fig. 1) at 1776 cm.$^{-1}$ shows the presence of the γ-lactone ring. The formation of this lactone ester proves conclusively the structure of the endo adduct.

EXPERIMENTAL

Preparation of adducts

Purified β-naphthol (9 gm.) and pure maleic anhydride (6 gm.) were heated at 220–40° C. in a conical flask placed in a Wood's alloy metal-bath for half an hour. After cooling, the products were dissolved in the minimum quantity of hot ethyl acetate and allowed to crystallise slowly. Crystals obtained melted at 152–58° C. (4·5 gm.). On recrystalling thrice from ethyl acetate, pure crystals of the exo-form (1·5 gm.) melting sharply at 193–94° C.

were obtained. Careful recrystallisations of the residues from the above yielded the endo-form (0·4 gm.) melting at 192–93° C. (mixed melting point with the exo-form 152–55° C.).

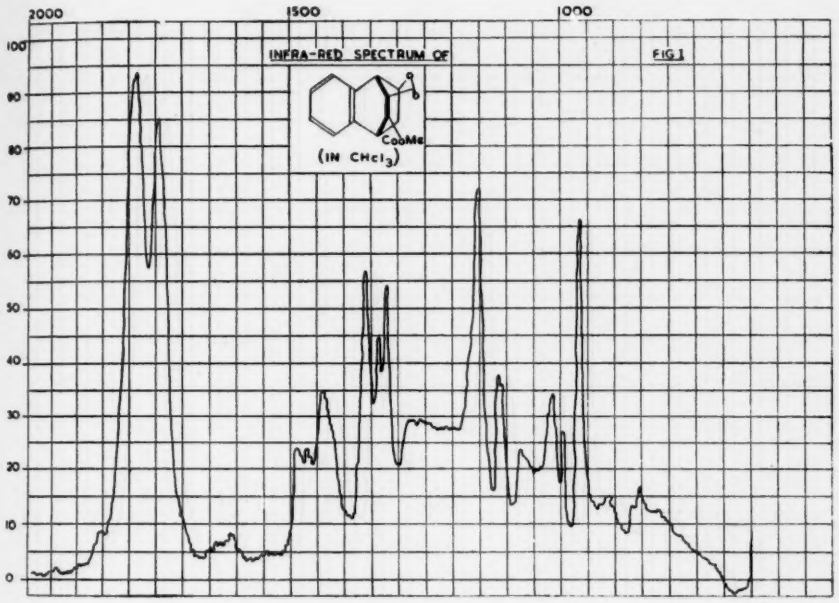


FIG. 1

Incidentally it was found that the mixed anhydrides could be converted into the dicarboxylic acids by heating with water and separated into the exo acid and endo acid easily. The former, unlike the latter, was only slightly soluble in ether.

Conversion of the adducts into the dimethyl ester

The dicarboxylic acids (0·5 gm. each) were dissolved in methyl alcohol (5 c.c.) and an ethereal solution of diazomethane was added until a yellow colour persisted. The yellow colour was then destroyed with a few drops of glacial acetic acid. On concentrating the solutions and cooling, crystals of the dimethyl ester separated (0·40 gm.). On recrystallisation from methanol, the exo-ester melted at 96–97° C. and the endo-ester at 112–13° C. The ultra-violet spectrum of the anhydrides (Figs. 1 and 2)—$\lambda_{max.}$ of exo=297 $m\mu$ and $\epsilon = 305{\cdot}8$ and $\lambda_{max.}$ of endo=299 $m\mu$ and $\epsilon = 338$ as well as the melting points of the esters show indentity with the values given by Takeda *et al.*

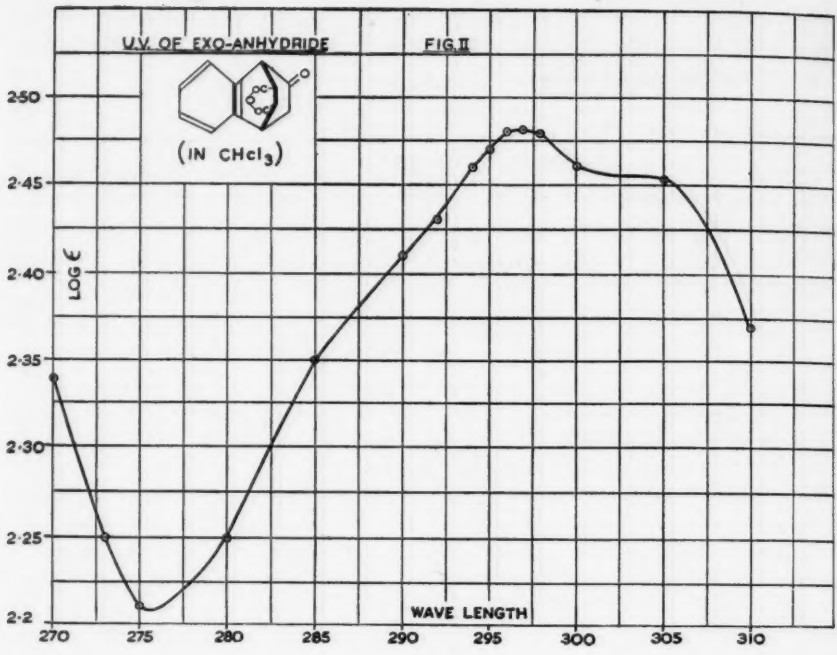


FIG. 2

The anomalous, long wave-length band in the U.V. spectrum due to the interaction between the carbonyl group and the benzene ring will be discussed elsewhere.

Reduction of the esters

(A) *Exo-ester.*—The ester (0·70 gm.) was dissolved in methanol (10 ml.) and sodium borohydride (0·5 gm.) was added in small quantities. A vigorous reaction took place. After two hours, water was added and then extracted with chloroform. On removal of the chloroform, an oil (·50 gm.) was obtained. The oil was dissolved in 95 per cent. ethanol and cooled. Colourless crystals melting at 118–19° C. were obtained. Recrystallisation from alcohol gave needles melting at 128–29° C. $C_{16}H_{18}O_5$ requires C = 66·20 per cent.; H=6·21 per cent. Found: C = 66·32%, H = 6·24%.

(B) *Endo-ester.*—The ester (0·75 gm.) was dissolved in methanol (10 ml.) and worked up exactly as in the above case. Pure crystals (0·25 gm.) melting at 128–29° C. were obtained. Mixed melting point with the reduction

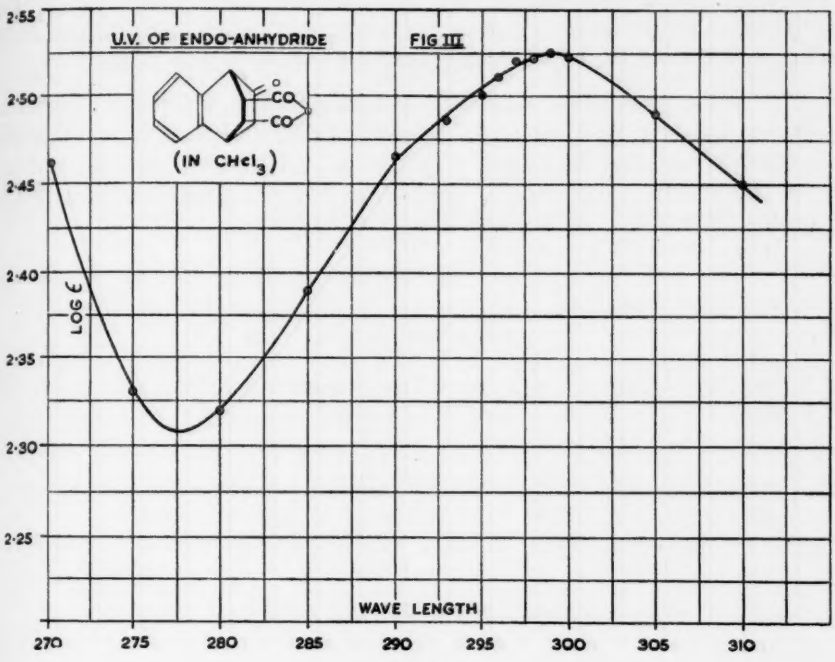


FIG. 3

product of the exo-ester was 95–97° C. $C_{15}H_{14}O_4$ requires C = 69·75%, H = 5·46%. Found: C = 69·76%, H = 5·37%.

Reduction of the endo-dicarboxylic acid

The acid (1·0 gm.) was dissolved in aqueous methanol and potassium borohydride (2·0 gm.) was added in small quantities. A vigorous reaction followed. After two hours, the resulting solution was just acidified with glacial acetic acid. The solid, which separated, was filtered out and the filtrate heated with a few drops of concentrated hydrochloric acid. On allowing the solution to cool, needle-shaped crystals (0·3 gm.) separated. Recrystallised from aqueous methanol the lactone acid melted at 198–200° C. $C_{14}H_{12}O_4$ requires C = 68·85%, H = 4·92%. Found: C = 68·88%, H = 4·97%.

These crystals (0·2 gm.) were dissolved in methanol and esterified with diazomethane in ether in the usual way. On removing most of the solvents and leaving overnight, crystals melting at 114–16° C. (0·10 gm.) were

obtained. After recrystallisation from methanol, these melted at 128° C., and gave no depression in melting point with the lactone ester obtained from the reduction of the endo-dimethyl ester by sodium borohydride.

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REFERENCES

1. Takeda and Kitabonoki .. *J. Pharm. Soc.*, Japan, 1951, **71**, 860.
2. —, Nagakura and Kitabonoki *Pharm. Bull.*, 1953, **1**, 135–38.
3. Kwart and Kaplan .. *J. Amer. Chem. Soc.*, 1953, **75**, 3356.
4. Berson .. *Ibid.*, 1954, **76**, 4069.

ON THE STEADY LAMINAR FLOW OF CERTAIN NON-NEWTONIAN LIQUIDS THROUGH AN ELASTIC TUBE

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1. Introduction

The flow of a viscous imcompressible fluid in an elastic tube has been studied by Rashevsky (1945) and Morgan (1952). Morgan has examined the conditions under which an approximate relation between the radius of the tube and the distance along the axis is consistent with the assumptions made in the solution. The solution obtained is limited to Newtonian liquids and do not give any information about the effect of cross-viscosity which is present in a number of highly viscous fluids of technological and biomathematical importance.

In this paper the flow of certain non-Newtonian liquids through an elastic tube is studied by considering the general Reiner-Rivlin stress-strain-velocity isotropic relations instead of stress-strain relations of classical Hydrodynamics. The most general form of such relations is obtained by introducing second degree terms of the type $d_a{}^i d_j{}^a$ into the classical relations. The conditions are examined under which an approximate relation between the radius of the tube and the distance along the axis is consistent with the assumptions made in the solution. These conditions are reduced to the relation between three dimensionless parameters. Second approximations are considered for different ranges of values of these parameters. It is found that the effect of cross-viscosity is to increase the radius of the tube with the distance along the axis.

2. Equations of Motion

The equations of motion proposed by Reiner (1952) for non-Newtonian liquids are

$$\rho\left(\frac{\partial v_i}{\partial t} + v_{i,j}v_j\right) = t^i{}_{j,j} + f^i, \tag{2.1}$$

$$t_j{}^i = -p\delta_j{}^i + \mathrm{F}_1 d_j{}^i + \mathrm{F}_2 d_a{}^i d_j{}^a, \tag{2.2}$$

$$v_{i,i} = 0, \tag{2.3}$$

where f^i is the body force, $2d_j{}^i = v_{i,j}+v_{j,i}$ is the strain velocity tensor, v_i is the velocity vector and ρ is the density (assumed constant), F_1 and F_2 are the two constants, known as the coefficients of viscosity and cross-viscosity respectively.

For the problem on hand it is convenient to use the cylindrical co-ordinate system r, θ, z in which r is the distance from the axis of the tube and z is the distance along the axis. The velocity components at any point are given by v_r, v_θ and v_z. On account of axial symmetry, the velocity component v_θ and its derivatives vanish.

The equation of continuity is:

$$\frac{1}{r}\frac{\partial (rv_r)}{\partial r} + \frac{\partial v_z}{\partial z} = 0. \tag{2·4}$$

The equation (2·4) can also be written in an integral form, *viz.*, that the total mass flow across any cross-section of radius $R(z)$ is constant and equal to say, Q:

$$2\pi\rho \int_0^{R(z)} rv_z dr = Q. \tag{2·5}$$

The equations of motion for axially symmetric, steady laminar flow of a non-Newtonian liquid become

$$\begin{aligned} v_r\frac{\partial v_r}{\partial r} + v_z\frac{\partial v_r}{\partial z} = &-\frac{1}{\rho}\frac{\partial p}{\partial r} + \nu\left[\frac{\partial^2 v_r}{\partial r^2} + \frac{1}{r}\frac{\partial v_r}{\partial r} + \frac{\partial^2 v_r}{\partial z^2} - \frac{v_r}{r^2}\right] \\ &+ \nu_1\left[8\frac{\partial^2 v_r}{\partial r^2}\cdot\frac{\partial v_r}{\partial r} + 2\frac{\partial^2 v_r}{\partial r\partial z}\cdot\frac{\partial v_r}{\partial z} + 2\frac{v_r}{r}\cdot\frac{\partial^2 v_r}{\partial r^2}\right. \\ &- \frac{6v_r{}^2}{r^3} + \frac{2v_r}{r^2}\cdot\frac{\partial v_r}{\partial r} + \frac{4}{r}\left(\frac{\partial v_r}{\partial r}\right)^2 + \frac{1}{r}\left(\frac{\partial v_r}{\partial z}\right)^2 \\ &- \frac{2}{r}\left(\frac{\partial v_r}{\partial z}\right)^2 - \frac{2v_r}{r}\cdot\frac{\partial^2 v_r}{\partial z^2} + \frac{1}{r}\left(\frac{\partial v_z}{\partial r}\right)^2 \\ &\left. + 2\frac{\partial v_r}{\partial z}\cdot\frac{\partial^2 v_z}{\partial r^2} + 2\frac{\partial v_z}{\partial r}\cdot\frac{\partial^2 v_z}{\partial r^2} + 2\frac{\partial^2 v_r}{\partial r\partial z}\cdot\frac{\partial v_z}{\partial r}\right], \end{aligned} \tag{2·6}$$

$$\begin{aligned} v_r\frac{\partial v_z}{\partial r} + v_z\frac{\partial v_z}{\partial z} = &-\frac{1}{\rho}\frac{\partial p}{\partial z} + \nu\left[\frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r}\frac{\partial v_z}{\partial r} + \frac{\partial^2 v_z}{\partial z^2}\right] \\ &+ \nu_1\left[8\frac{\partial^2 v_z}{\partial z^2}\cdot\frac{\partial v_z}{\partial z} + 2\frac{\partial^2 v_z}{\partial r\partial z}\cdot\frac{\partial v_z}{\partial r} + 2\frac{v_r}{r}\cdot\frac{\partial^2 v_z}{\partial z^2}\right. \\ &\left. + \frac{2v_r}{r^2}\cdot\frac{\partial v_r}{\partial z} - \frac{2v_r}{r}\cdot\frac{\partial^2 v_z}{\partial r^2} + \frac{2v_r}{r^2}\cdot\frac{\partial v_z}{\partial r}\right. \end{aligned}$$

$$+\frac{2}{r}\cdot\frac{\partial v_z}{\partial r}\cdot\frac{\partial v_z}{\partial z}-\frac{2}{r}\cdot\frac{\partial v_r}{\partial z}\cdot\frac{\partial v_r}{\partial r}$$

$$+2\frac{\partial v_r}{\partial z}\cdot\frac{\partial^2 v_r}{\partial z^2}+2\frac{\partial v_r}{\partial z}\cdot\frac{\partial^2 v_z}{\partial r\partial z}+2\frac{\partial v_z}{\partial r}\cdot\frac{\partial^2 v_r}{\partial z^2}\Big], \qquad (2\cdot7)$$

where p is the pressure (for convenience p is taken as the difference between the fluid pressure and the constant pressure outside the tube), $\nu=\mu/\rho$, $\nu_1=\mu_1/\rho$ are the Kinematic coefficients of viscosity and cross-viscosity respectively. On using (2·2) the normal compressive force per unit area perpendicular to a radius is given by

$$\mathrm{E}_{rr}(r,z)=p-2\mu\frac{\partial v_r}{\partial r}-4\mu_1\Big[\Big(\frac{\partial v_r}{\partial r}\Big)^2+\frac{1}{4}\Big(\frac{\partial v_r}{\partial z}+\frac{\partial v_z}{\partial r}\Big)^2\Big]. \qquad (2\cdot8)$$

Equation of Elasticity

If R varies very slowly with z and if we neglect effects at the ends of the tube, then the forces in the tube will have no component parallel to the axis. The following equation can be derived, provided δ the wall thickness, is very small compared to R:

$$\mathrm{E}_{rr}(\mathrm{R},z)=\mathrm{E}\delta\Big(\frac{1}{\mathrm{R}_u}-\frac{1}{\mathrm{R}}\Big), \qquad (2\cdot9)$$

where E is Young's modulus, R_u is the unstretched radius of the tube (subsequently assumed to be constant) and E_{rr} represents the difference between the normal compressive stress on the interior of the tube and the external pressure.

In this derivation we have neglected the effect on the radius R (z) of the fluid friction on the interior of the tube, and that, due to the slow variation of R (z), we take the component of E_{rr} which is normal to the wall to be equal to E_{rr} itself.

3. Solution of the Equations of Motion

First approximation.—Since R (z) varies very slowly with z, we can to a first approximation neglect all terms containing v_r and its derivatives. We will investigate under what conditions this assumption may be expected to yield reasonable results. Equation (2·6) becomes

$$\frac{\partial p}{\partial r}=\mu_1\Big[\frac{1}{r}\Big(\frac{\partial v_z}{\partial r}\Big)^2+\frac{\partial}{\partial r}\Big(\frac{\partial v_z}{\partial r}\Big)^2\Big].$$

Now neglecting $\left(\frac{\partial v_z}{\partial r}\right)^2$ we get

$$\frac{\partial p}{\partial r} = 0,$$

i.e.,

$$p = p(z).$$

Hence from (2·8) it follows that

$$E_{rr}(R, z) = p(z).$$

Then (2·9) gives

$$\frac{dp}{dz} = \frac{E\delta}{R^2}\frac{dR}{dz}, \tag{3.1}$$

and equation (2·7) can now be written

$$\frac{1}{\rho}\frac{dp}{dz} = \nu\left(\frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r}\frac{\partial v_z}{\partial r}\right), \tag{3.2}$$

provided we neglect the terms

$$v_r\frac{\partial v_z}{\partial r} + v_z\frac{\partial v_z}{\partial z}, \qquad \nu\frac{\partial^2 v_z}{\partial z^2}, \qquad \nu_1\frac{\partial v_z}{\partial z}\cdot\frac{\partial^2 v_z}{\partial z^2},$$

$$\nu_1\frac{\partial v_z}{\partial r}\cdot\frac{\partial^2 v_z}{\partial r\,\partial z}, \qquad \frac{\nu_1}{r}\cdot\frac{\partial v_z}{\partial r}\cdot\frac{\partial v_z}{\partial z}.$$

The integration of (3·2) and the application of the boundary condition $v_z = 0$ at $r = R$ yields

$$v_z = -\frac{1}{4\mu}\frac{dp}{dz}\left[R^2(z) - r^2\right]. \tag{3.3}$$

For any fixed z this equation gives a parabolic radial distribution for v_z as in the case of classical viscous fluid.

Substituting (3·1) into (3·3) we obtain

$$v_z = -\frac{E\delta}{4\mu}\frac{dR}{dz}\left[1 - \frac{r^2}{R^2}\right]. \tag{3.4}$$

If we now apply equation (2·5), we obtain

$$\frac{dR}{dz} = \frac{-8\mu Q}{E\delta\pi\rho R^3} \tag{3.5}$$

and

$$\frac{R^3}{3} = \frac{R_0^3}{3} - \frac{8\mu Q}{E\delta\pi\rho}z, \tag{3.6}$$

as was obtained by Morgan (1952) and Rashevsky (1945) in the case of classical viscous fluid, R_0 being the radius at $z = 0$.

Validity of the approximation.—We have neglected certain terms in equation (2·7). We will now examine under what circumstances the above solution is consistent with the assumptions.

Now from equations (3·1), (3·2) and (3·5) we have

$$\nu\left(\frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r}\frac{\partial v_z}{\partial r}\right) = \frac{-8\mu Q}{\pi\rho^2 R^4}.$$

The terms neglected are

$$v_r \frac{\partial v_z}{\partial r} = O\left(\frac{\mu Q^3}{E\delta\rho^3 R^7}\right),$$

$$v_z \frac{\partial v_z}{\partial z} = O\left(\frac{\mu Q^3}{E\delta\rho^3 R^7}\right),$$

$$\nu \frac{\partial^2 v_z}{\partial z^2} = O\left(\frac{\mu^3 Q^3}{E^2\delta^2\rho^4 R^8}\right),$$

$$\nu_1 \frac{\partial v_z}{\partial r}\cdot\frac{\partial^2 v_z}{\partial r\partial z} = O\left(\frac{\mu\mu_1 Q^3}{E\delta\rho^4 R^9}\right),$$

$$\nu_1 \frac{1}{r}\cdot\frac{\partial v_z}{\partial r}\cdot\frac{\partial v_z}{\partial z} = O\left(\frac{\mu\mu_1 Q^3}{E\delta\rho^4 R^9}\right),$$

$$\nu_1 \frac{\partial v_z}{\partial z}\cdot\frac{\partial^2 v_z}{\partial z^2} = O\left(\frac{\mu^3\mu_1 Q^5}{E^3\delta^3\rho^6 R^{13}}\right).$$

Hence we may neglect $v_r \frac{\partial v_z}{\partial r}$ and $v_z \frac{\partial v_z}{\partial z}$ provided

$$\frac{Q^2}{E\delta\rho R^3} \ll 1. \tag{3·7}$$

If we may write $Q = \rho V R^2$ where V is the average velocity over a cross-section, we have

$$\frac{\rho V^2 R}{E\delta} \ll 1. \tag{3·8}$$

We may neglect the term $\nu \frac{\partial^2 v_z}{\partial z^2}$ provided

$$\frac{Q^2\mu^2}{E^2\delta^2\rho^2 R^4} \ll 1, \tag{3·9}$$

or

$$\left(\frac{\mu V}{E\delta}\right)^2 \ll 1. \tag{3·10}$$

We may neglect the terms

$$\nu_1 \frac{\partial v_z}{\partial r}\cdot\frac{\partial^2 v_z}{\partial r \partial z} \quad \text{and} \quad \frac{\nu_1}{r}\cdot\frac{\partial v_z}{\partial r}\cdot\frac{\partial v_z}{\partial z},$$

provided

$$\frac{\mu_1 Q^2}{E\delta\rho^2 R^5} \ll 1, \tag{3·11}$$

or

$$\frac{\mu_1 V^2}{E\delta R} \ll 1. \tag{3·12}$$

We may neglect the term $\nu_1 \frac{\partial v_z}{\partial z}\cdot\frac{\partial^2 v_z}{\partial z^2}$ provided,

$$\frac{\mu^2\mu_1 Q^4}{E^3\delta^3\rho^4 R^9} \ll 1, \tag{3·13}$$

or

$$\frac{\mu^2\mu_1 V^4}{E^3\delta^3 R} \ll 1. \tag{3·14}$$

Now if we write $\frac{\rho VR}{\mu} = \mathscr{R}_1$, a Reynolds number appropriate to our problem (V and R may be taken to be the values at $z = 0$) and

$$\frac{\mu V}{E\delta} = \mathscr{R}_2, \qquad \frac{\mu_1 V^2}{E\delta R} = \mathscr{R}_3,$$

the conditions (3·8), (3·10), (3·12) and (3·14) reduce respectively to

$$\mathscr{R}_1\mathscr{R}_2 \ll 1,\ \mathscr{R}_2^2 \ll 1,\ \mathscr{R}_3 \ll 1,\ \mathscr{R}_2^2\mathscr{R}_3 \ll 1.$$

But these reduce to only three conditions

$$\mathscr{R}_1\mathscr{R}_2 \ll 1, \tag{3·15}$$

$$\mathscr{R}_2^2 \ll 1, \tag{3·16}$$

$$\mathscr{R}_3 \ll 1. \tag{3·17}$$

$\mathscr{R}_2$ and $\mathscr{R}_3$ are non-dimensional parameters. $\mathscr{R}_2$ = ratio of a viscous to an elastic force. $\mathscr{R}_3$ = ratio of a cross-viscous to an elastic force. We regard $\mathscr{R}_1$, $\mathscr{R}_2$ and $\mathscr{R}_3$ as the three dimensionless parameters of the system.

For any fixed $\mathscr{R}_1$, the flow will approach Poiseuille flow as $\mathscr{R}_2$ and $\mathscr{R}_3 \to 0$.

Now considering equation (2·8) we can write

$$\frac{\partial E_{rr}}{\partial z} = \frac{\partial p}{\partial z}, \quad \text{provided}$$

$$\left| \mu \frac{\partial^2 v_r}{\partial r \partial z} \right| \ll \left| \frac{\partial p}{\partial z} \right|,$$

$$\left| \mu_1 \frac{\partial v_r}{\partial r} \cdot \frac{\partial^2 v_r}{\partial r \partial z} \right| \ll \left| \frac{\partial p}{\partial z} \right|,$$

and

$$\left| \mu_1 \left(\frac{\partial v_r}{\partial z} + \frac{\partial v_z}{\partial r} \right) \left(\frac{\partial^2 v_r}{\partial z^2} + \frac{\partial^2 v_z}{\partial r \partial z} \right) \right| \ll \left| \frac{\partial p}{\partial z} \right|,$$

i.e., provided $\mathscr{R}_2^2 \ll 1$, $\mathscr{R}_2^2 \mathscr{R}_3 \ll 1$ and $\mathscr{R}_3 \ll 1$, which have already been obtained as conditions. Hence we are justified in writing $\frac{\partial E_{rr}}{\partial z} = \frac{\partial p}{\partial z}$ as in the case of classical viscous fluid.

Using equation (2·6), we have,

$$\frac{1}{\rho} \frac{\partial p}{\partial r} = -\frac{2\nu Q}{\pi \rho} \cdot \frac{dR}{dz} \left(\frac{8r}{R^5} \right) + \text{higher order terms.}$$

By integrating from r to R and using (2·9) we get

$$p(r, z) = E\delta \left(\frac{1}{R_u} - \frac{1}{R} \right) + \frac{8\mu Q}{\pi \rho} \frac{dR}{dz} \left(\frac{1}{R^3} - \frac{r^2}{R^5} \right). \tag{3·18}$$

By differentiating this equation (3·18) with respect to z we get

$$\frac{\partial p}{\partial z} = \frac{E\delta}{R^2} \frac{dR}{dz} + \frac{8\mu Q}{\pi \rho} \left(\frac{dR}{dz} \right)^2 \left(-\frac{3}{R^4} + \frac{5r^2}{R^6} \right) + \frac{8\mu Q}{\pi \rho} \frac{d^2R}{dz^2} \left(\frac{1}{R^3} - \frac{r^2}{R^5} \right). \tag{3·19}$$

Thus the expression for $\frac{\partial p}{\partial z}$ will be the same as was obtained by Morgan (1952) in the case of classical viscous liquid. The last two terms in equation (3·19) are negligible in comparison with the first term provided $\mathscr{R}_2^2 \ll 1$, which is the condition already obtained.

Second approximation.—We will consider three cases for ranges of values of the three dimensionless parameters of the system.

Cases: $\mathscr{R}_1 \gg 1$, $\mathscr{R}_1 \mathscr{R}_2 \ll 1$, $\mathscr{R}_3 \ll 1$.

and $\mathscr{R}_1 = O(1)$, $\mathscr{R}_2 \ll 1$, $\mathscr{R}_3 \ll 1$.

In these cases we will have to take account of some of the terms previously neglected, by evaluating them with the help of the first approximation. Calling the terms retained in the first approximation, terms of order one, the next higher order terms in these cases will be those of order $\mathscr{R}_1\mathscr{R}_2$, *i.e.*, the quadratic terms in (2·7). These terms have the same approximate value as in the case of classical viscous liquid. That is,

$$v_r \frac{\partial v_z}{\partial r} + v_z \frac{\partial v_z}{\partial z} = \mathrm{I}(r, z) = \frac{8\mathrm{Q}^2}{\pi^2\rho^2} \frac{d\mathrm{R}}{dz}\left(-\frac{r^4}{\mathrm{R}^9} + \frac{2r^2}{\mathrm{R}^7} - \frac{1}{\mathrm{R}^5}\right). \quad (3\cdot20)$$

Hence (2·7) in this second approximation becomes

$$\mathrm{I}(r, z) = -\frac{1}{\rho}\frac{\partial p}{\partial z} + \nu\left(\frac{\partial^2 v_z}{\partial z^2} + \frac{1}{r}\frac{\partial v_z}{\partial r}\right). \quad (3\cdot21)$$

Integrating this and applying the boundary condition $v_z = 0$ at $r = \mathrm{R}$, we obtain as Morgan (1952) has done in the case of classical viscous liquid,

$$v_z = -\frac{\mathrm{E}\delta}{4\mu}\frac{d\mathrm{R}}{dz}\left(1 - \frac{r^2}{\mathrm{R}^2}\right) + \frac{2\mathrm{Q}^2}{\pi^2\rho\mu}\frac{d\mathrm{R}}{dz}\left(-\frac{r^6}{9\mathrm{R}^9} + \frac{r^4}{2\mathrm{R}^7} - \frac{r^2}{\mathrm{R}^5} + \frac{11}{18\mathrm{R}^3}\right). \quad (3\cdot22)$$

Now applying (2·5) we arrive at the same equation for $\frac{d\mathrm{R}}{dz}$ as was obtained by Morgan (1952) in the case of classical viscous liquid, *viz.*,

$$\left(-\frac{\mathrm{E}\delta\pi\rho}{8\mu\mathrm{Q}}\mathrm{R}^2 + \frac{\mathrm{Q}}{2\pi\mu}\frac{1}{\mathrm{R}}\right)\frac{d\mathrm{R}}{dz} = 1. \quad (3\cdot23)$$

Since $\frac{d\mathrm{R}}{dz}$ is negative, the effect of the second term in parenthesis is to diminish the radius R more rapidly. It is to be noted that, since the conditions (3·7), (3·9) and (3·11) involve the variable R the equations hold only over a range of z in which R does not become too small.

Case: $\mathscr{R}_1 \ll 1$, $\mathscr{R}_2 = \mathrm{O}(\mathscr{R}_1)$ and $\mathscr{R}_3 = \mathrm{O}(\mathscr{R}_1)$.

In this case we must take account of terms of order $\mathscr{R}_1\mathscr{R}_2$, $\mathscr{R}_2^2$ and $\mathscr{R}_3$, *i.e.*, all the terms previously neglected in (2·7) and (2·8). We will follow, as before, the method of successive approximations, *i.e.*, by replacing all unknown terms of second order by their approximate values as obtained from the first approximation.

The equation (2·7) becomes

$$\frac{8\mathrm{Q}^2}{\pi^2\rho^2}\frac{d\mathrm{R}}{dz}\left[-\frac{r^4}{\mathrm{R}^9} + \frac{2r^2}{\mathrm{R}^7} - \frac{1}{\mathrm{R}^5}\right] = -\frac{1}{\rho}\frac{\partial p}{\partial z} + \nu\left[\frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r}\frac{\partial v_z}{\partial r}\right]$$
$$+ \nu\frac{d\mathrm{R}}{dz}\left[-\frac{160\mu\mathrm{Q}^2}{\mathrm{E}\delta\pi^2\rho^2\mathrm{R}^6} + \frac{448\mu\mathrm{Q}^2r^2}{\mathrm{E}\delta\pi^2\rho^2\mathrm{R}^8}\right]$$
$$- \frac{32\mu\nu_1\mathrm{Q}^3}{\pi^2\rho^2}\frac{d\mathrm{R}}{dz}\left[-\frac{1}{\mathrm{R}^7} + \frac{6r^2}{\mathrm{R}^9}\right]. \quad (3\cdot24)$$

Now equations (2·6), (2·8) and (2·9) yield the following expression for p:

$$p(r,z) = \mathrm{E}\delta\left(\frac{1}{\mathrm{R}_u} - \frac{1}{\mathrm{R}}\right) + \frac{8\mu\mathrm{Q}}{\pi\rho}\frac{d\mathrm{R}}{dz}\left(\frac{1}{\mathrm{R}^3} - \frac{r^2}{\mathrm{R}^5}\right) + \frac{64\mu^2\mathrm{Q}^2}{\mathrm{E}\delta\pi^2\rho^2\mathrm{R}^5} + \frac{64\mu\mathrm{Q}^3}{\mathrm{E}\delta\pi^3\rho^2}\frac{d\mathrm{R}}{dz}\left(\frac{1}{\mathrm{R}^6} - \frac{r^2}{\mathrm{R}^8}\right) + \frac{16\mu_1\mathrm{Q}^2r^2}{\pi^2\rho^2\mathrm{R}^8} + \frac{3\mathrm{QE}\delta\mu_1}{\pi\rho\mu}\cdot\frac{d\mathrm{R}}{dz}\left(\frac{1}{\mathrm{R}^4} - \frac{r^2}{\mathrm{R}^6}\right). \quad (3\cdot25)$$

Hence

$$\frac{\partial p}{\partial z} = \frac{\mathrm{E}\delta}{\mathrm{R}^2}\frac{d\mathrm{R}}{dz} + \frac{8\mu\mathrm{Q}}{\pi\rho}\left(\frac{d\mathrm{R}}{dz}\right)^2\left(-\frac{3}{\mathrm{R}^4} + \frac{5r^2}{\mathrm{R}^6}\right) + \frac{8\mu\mathrm{Q}}{\pi\rho}\frac{d^2\mathrm{R}}{dz^2}\left(\frac{1}{\mathrm{R}^3} - \frac{r^2}{\mathrm{R}^5}\right) - \frac{320\mu^2\mathrm{Q}^2}{\mathrm{E}\delta\pi^2\rho^2\mathrm{R}^6}\frac{d\mathrm{R}}{dz} + \frac{3\mathrm{QE}\delta\mu_1}{\pi\rho\mu}\left(\frac{d\mathrm{R}}{dz}\right)^2\left(-\frac{4}{\mathrm{R}^5} + \frac{6r^2}{\mathrm{R}^7}\right) + \frac{3\mathrm{QE}\delta\mu_1}{\pi\rho\mu}\frac{d^2\mathrm{R}}{dz^2}\left(\frac{1}{\mathrm{R}^4} - \frac{r^2}{\mathrm{R}^6}\right). \quad (3\cdot26)$$

If we introduce this expression (3·26) for $\frac{\partial p}{\partial z}$ into (3·24) and perform the integration, applying the boundary condition, *viz.*, when $r = \mathrm{R}$, $v_z = 0$, then we get by expressing $\frac{d^2\mathrm{R}}{dz^2}$ and $\left(\frac{d\mathrm{R}}{dz}\right)^2$ in terms of $\frac{d\mathrm{R}}{dz}$,

$$v_z = -\frac{\mathrm{E}\delta}{4\mu}\frac{d\mathrm{R}}{dz}\left(1 - \frac{r^2}{\mathrm{R}^2}\right) + \frac{2\mathrm{Q}^2}{\pi^2\rho\mu}\frac{d\mathrm{R}}{dz}\left(-\frac{r^6}{9\mathrm{R}^9} + \frac{r^4}{2\mathrm{R}^7} - \frac{r^2}{\mathrm{R}^5} + \frac{11}{18\mathrm{R}^3}\right) + \frac{8\mu\mathrm{Q}^2}{\mathrm{E}\delta\pi^2\rho^2}\frac{d\mathrm{R}}{dz}\left(-\frac{7r^4}{\mathrm{R}^8} + \frac{5r^2}{\mathrm{R}^6} + \frac{2}{\mathrm{R}^4}\right) + \frac{4\mu_1\mathrm{Q}^2}{\pi^2\rho^2\mu}\frac{d\mathrm{R}}{dz}\left(-\frac{5r^4}{\mathrm{R}^9} + \frac{9r^2}{\mathrm{R}^7} - \frac{4}{\mathrm{R}^5}\right) + \frac{4\mu_1\mathrm{Q}^3}{\pi^2\rho^2}\frac{d\mathrm{R}}{dz}\left(\frac{3r^4}{\mathrm{R}^9} - \frac{2r^2}{\mathrm{R}^7} - \frac{1}{\mathrm{R}^5}\right). \quad (3\cdot27)$$

Now the application of equation (2·5) will yield the equation

$$\frac{d\mathrm{R}}{dz}\left[-\frac{\mathrm{E}\delta\pi\rho}{8\mu\mathrm{Q}}\mathrm{R}^2 + \frac{\mathrm{Q}}{2\pi\mu}\frac{1}{\mathrm{R}} + \frac{52}{3}\frac{\mu\mathrm{Q}}{\mathrm{E}\delta\pi\rho}\frac{1}{\mathrm{R}^2} - \frac{14}{3}\frac{\mu_1\mathrm{Q}}{\pi\rho\mu}\frac{1}{\mathrm{R}^3} - \frac{4\mu_1\mathrm{Q}^2}{\pi\rho}\frac{1}{\mathrm{R}^5}\right] = 1. \quad (3\cdot28)$$

The last two terms in parenthesis in equation (3·28) are the cross-viscous terms. While the effect of inertial forces and viscosity is to diminish the radius of the tube, the effect of cross-viscosity is to increase the radius of the tube with the distance along the axis. Thus it is seen that the effect of cross-viscosity compensates to some extent the effect of viscosity and inertial forces in flow of a liquid through an elastic tube. Prof. G. W. Morgan has kindly pointed out to me that the influence of Poisson's ratio on the shape of the tube might be as important as the effect of cross-viscosity. Since the purpose of our problem is to investigate only the effect of cross-viscosity on the shape of the elastic tube this effect has not been taken into consideration.

SUMMARY

This paper is a study of the effect of cross-viscosity on the radius of an elastic tube when certain highly viscous non-Newtonian liquids flow through it under pressure gradient. The effect is found to be of opposite nature to that of inertial and viscous forces and causes the radius of the tube to increase with the distance along the axis.

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In conclusion, I thank Prof. B. R. Seth, for his kind guidance throughout this work.

REFERENCES

1. Morgan, G. W. .. *Bull. Math. Biophysics*, 1952, **14**, No. 1.
2. Rashevsky, N. .. *Ibid.*, 1945, **7**, 35.
3. Reiner, M, .. *Quarterly Journal of Mech. and Applied Math.*, 1952, **5**, 42.

ON THE PHENOMENOLOGICAL THEORY OF LIGHT PROPAGATION IN OPTICALLY ACTIVE CRYSTALS

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1. Introduction

The treatment customarily adopted[1] for analysing the propagation of light in optically active crystals is somewhat lengthy and cumbersome, and is even so not free from approximation: its mathematical complexity being perhaps partly the reason why an alternative quasi-theoretical analysis not involving the electromagnetic theory is sometimes used.[2,3] A concise yet logical treatment of the problem is, however, easily possible without the introduction of any fresh physical hypothesis—as will be shown in this paper.

We have merely to remember that for an electromagnetic wave inside a crystal, it is the dielectric displacement vector **D** (the ' vibration '), and not the electric intensity **E** which necessarily lies on the wave-front. Hence we seek to express **E** in terms of **D**, rather than *vice-versa*. Even for the case of optically inactive crystals, such a procedure—though not commonly adopted—is known to simplify the theoretical treatment, as may be seen especially in the case of absorbing crystals[4]; and the geometric representation of the optical properties of a crystal by an *index ellipsoid* follows directly in the structure of such a presentation instead of having to be proved by indirect means later—as is usually done.[5]

2. Formulation of the Problem

Any wave travelling in the crystal along an arbitrary direction ' z ' (conveniently taken as being normal to the plane of the paper) may be specified by giving the x and y components of the D-vibration: $D_x \exp i\omega(t - z/v)$ and $D_y \exp i\omega(t - z/v)$. Here v is the velocity of the wave and the ratio (D_y/D_x) completely defines the polarisation of the wave. Owing to the requirement that the vectors **D** and **E** must satisfy both Maxwell's relations as well as the characteristic polarisable property of the medium, only two specific waves can be propagated in the z-direction—the problem being to determine their velocities, v_1 and v_2, and their states of polarisation $(D_y/D_x)_1$ and $(D_y/D_x)_2$.

Maxwell's equations for a plane-wave field reduce to the following single equation when **H** is eliminated*—as is shown in standard texts[7]

$$v^2\mathbf{D} = c^2\,[\mathbf{E} - \mathbf{s}\,(\mathbf{E}.\mathbf{s})] \tag{1}$$

where **s** is a unit-vector along the wave-normal. For inactive crystals the polarisable characteristics of the medium lead to the usual relation $\mathbf{D} = (\epsilon)\,\mathbf{E}$, where (ϵ) represents the symmetric dielectric tensor—which operates on **E** to give **D**. But for optically active media it is assumed that

$$\mathbf{D} = (\epsilon)\,\mathbf{E} + i\,\mathbf{G}\times\mathbf{E} \tag{2}$$

where the additional antisymmetric term represents a feeble additional polarisation which oscillates out of phase with the electric intensity (as indicated by the factor i), and yet does not introduce any absorption because it is also orthogonal to the electric intensity (as is indicated by the occurrence of the vector product). The *gyration-vector* **G** corresponding to the direction of propagation **s** determines the optical rotatory power in that direction.

3. THE INVERSE GYRATION-VECTOR

It is known that by taking the z-axis along the wave-normal (instead of choosing co-ordinate axes along the electrical axes, as in usual treatments), we not only confine ourselves to two components of **D** instead of three; in addition, the components of the vector equation (1) take the following intelligible form:

$$v^2\mathbf{D}_x = c^2\mathbf{E}_x;\;\; v^2\mathbf{D}_y = c^2\mathbf{E}_y;\;\; D_z = 0 \tag{1\,a}$$

where, it may be noted, separate and explicit expressions are obtained for $\mathbf{E}_x$ and $\mathbf{E}_y$.

Equation (2) which expresses **D** as a vector function of **E**, is now transformed by expressing **E** in terms of **D** using the inverse vector function. Since this inverse function will obviously contain not only a real symmetric part but also an imaginary antisymmetric part (giving that part of the electric intensity which oscillates out of phase with **D**, and is orthogonal to it), we may write

$$c^2\mathbf{E} = (a)\,\mathbf{D} - i\,\boldsymbol{\Gamma}\times\mathbf{D} \tag{2\,a}$$

The first term alone would be present for an optically inactive crystal, the symmetric tensor (a) then defining the *index ellipsoid*†—being proportional to the inverse of the dielectric tensor (see Appendix). The comparatively

* We are not here considering other theories of optical activity[2,6] in which $\mathbf{B} \neq \mathbf{H}$.

† If $a_{11}x^2 + a_{22}y^2 + \ldots . 2a_{31}\,zx = 1$, be the equation to the index ellipsoid, then the a_{ij} are also the components of the tensor (a) with respect to the co-ordinate axes chosen.

small second term (which introduces the optical activity) is determined by the new vector Γ—which we shall refer to as the inverse gyration-vector corresponding to the direction of propagation s.

4. Derivation of the Equations of Wave-Propagation

Writing down the x and y components of equation (2 *a*) and omitting the terms containing the factor D_z (since $D_z = 0$):

$$\left.\begin{aligned} c^2E_x &= a_{11}D_x + a_{12}D_y + i\Gamma_z D_y \\ c^2E_y &= a_{22}D_y + a_{12}D_x - i\Gamma_z D_x \end{aligned}\right\} \tag{3}$$

Here $a_{11}x^2 + a_{22}y^2 + 2a_{12}xy = 1$, is the equation to the elliptical section of the index ellipsoid taken perpendicular to the wave-normal. We now choose the x and y axes parallel to the principal radii of this elliptical section, which represent the vibration-directions in the absence of optical activity. *With this understanding* we may, in Equation (3), set $a_{12} = 0$, $a_{11} = v'^2$ and $a_{22} = v''^2$; here v' and v'' represent the velocities of the waves in the absence of optical activity, because of a well-known property of the index ellipsoid which may also be obtained by setting $\Gamma_z = 0$ at the end of the present discussion. Substituting for c^2E_x and c^2E_y from equation (1 *a*) we thus obtain as our fundamental equations:

$$\left.\begin{aligned} v^2 - v'^2 &= i\Gamma_z\left(\frac{D_y}{D_x}\right) \\ v^2 - v''^2 &= -i\Gamma_z\left(\frac{D_x}{D_y}\right) \end{aligned}\right\} \tag{4}$$

These fundamental equations are essentially the same as those obtained in Pockel's *Lehrbuch*[2] starting from an entirely different theory of optical activity. There are two pairs of roots v_1, $(D_y/D_x)_1$ and v_2, $(D_y/D_x)_2$, which simultaneously satisfy these equations—giving thereby the required velocities and states of polarisation.

5. The Velocities and States of Polarisation of the Waves

Multiplying the two equations of (4) to eliminate (D_y/D_x) we obtain the following quadratic in v^2, whose roots v_1^2 and v_2^2 give the velocities of the waves:

$$(v^2 - v'^2)(v^2 - v''^2) = \Gamma_z^2 \tag{5}$$

Subtracting the second equation of (4) from the first to eliminate v^2, we get:

$$\frac{D_y}{D_x} + \frac{D_x}{D_y} = i\,\frac{v'^2 - v''^2}{\Gamma_z} \tag{6}$$

This is a quadratic in (D_y/D_x), and its roots uniquely determine the states of polarisation because of the relation:

$$\frac{D_y}{D_x} = \frac{|D_y|}{|D_x|}\,e^{iR}$$

where the ratio $|D_y| : |D_x|$ is obviously the ratio $\tan\theta$ of the (real) amplitudes of the y and x components of the D-vibration; and R is the relative phase difference between these components. Since the right-hand side of (6) is entirely imaginary it follows that both roots of the equation are imaginary ($R = \pm\pi/2$). Further since the roots of (6) are obviously reciprocals of one another, it follows that if one root is of the form $(B_1/A_1)\,e^{i\pi/2}$, the other will be $(A_1/B_1)\,e^{-i\pi/2}$. This signifies that both vibrations are elliptically polarised with their respective major axes along the two perpendicular principal planes, the vibrations being of the same ellipticity but traced in opposite senses.

The value of $\tan 2\theta$, which determines the common ellipticity of the two vibrations is obtained directly from equation (6) by substituting in it the value of (D_y/D_x) which is equal to $(+\,i\tan\theta_1)$ for the right elliptic vibration and $(-\,i\tan\theta_2)$ for the left elliptic vibration:

$$|\tan 2\theta| = |2\Gamma_z/(v'^2 - v''^2)| \tag{7}$$

Similarly the difference in the squares of the velocities of the two waves may be obtained from (5)—since it is the square-root of the discriminant:

$$(v_1^2 - v_2^2) = (v'^2 - v''^2) + (2\Gamma_z)^2 \tag{8}$$

In the absence of linear birefringence (*i.e.*, if we imagine $v' = v''$), the waves will be circularly polarised according to (7), the rotatory power ρ being obtained from (8) as:

$$\rho = (\omega/v_m^3) \cdot \Gamma_z \tag{9}$$

where v_m is a mean velocity (see Pockels[2]).

We may mention that because of an approximation made in the usual treatment, its resultant equations differ slightly from (5) and (6); also, equations (7) and (8) are the accurate forms of the approximate relations obtained by the method of superposition.[2,3]

6. The Variation of Rotatory Power with Direction

The gyration vector **G**, and hence in the present treatment the inverse gyration-vector $\boldsymbol{\Gamma}$, are both vectors not having their axes fixed with respect to the crystallographic axes,‡ but are linear vector functions of the direction of propagation. Thus $\mathbf{G} = (g)\,\mathbf{s}$ and $\boldsymbol{\Gamma} = (\gamma)\,\mathbf{s}$, where the gyration tensor (g) and hence the modified gyration tensor (γ) are both nine-component tensors. The rotatory power is however determined, according to (9), only by the resolved component Γ_s of the inverse gyration-vector along the direction of propagation. (We are here denoting this by Γ_s instead of Γ_z since we are choosing an arbitrary co-ordinate system $x'y'z'$.) Since an analogous result holds in the usual treatment it follows as in that case[6] that this scalar parameter of rotation Γ_s is a quadratic function of the direction cosines $l'm'n'$ of propagation:

$$\Gamma_s = \gamma_{11}l'^2 + \gamma_{22}m'^2 + \gamma_{33}n'^2 + 2\bar{\gamma}_{12}l'm' + 2\bar{\gamma}_{23}m'n' + 2\bar{\gamma}_{31}n'l'$$

where

$$\bar{\gamma}_{ij} = \tfrac{1}{2}(\gamma_{ij} + \gamma_{ji}), \qquad (i, j, = 1, 2, 3).$$

The discussion of optical activity in relation to crystal symmetry follows as in the usual treatment.

Finally, the author wishes to express his gratitude to Prof. Sir C. V. Raman, F.R.S., N.L., for his kind interest in this investigation.

7. Summary

In the usual treatment of the optical activity of crystals, the displacement vector of the light wave is expressed as a function of the electric vector—this being done with the aid of the dielectric tensor and the gyration-vector. The treatment is made more concise and tractable by using the inverse vector function and expressing the electric vector in terms of the displacement vector, since it is the latter which necessarily lies on the wave-front; this can be done by using the inverse of the dielectric tensor (which defines the index ellipsoid), and an inverse gyration-vector (which determines the rotatory power for the particular direction of propagation considered). The inverse gyration-vector (like the gyration-vector) is itself a function of the direction of propagation, being related to it by a modified gyration tensor—which consequently determines the rotatory power for all directions.

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‡ The new treatment given in Sommerfeld's *Optics*[5] is deficient in this respect.

8. REFERENCES

1. Szivessy .. *Handbuch der Physik*, Springer, 1928, Kap. 11, 810 *et seq.*
2. Pockels .. *Lehrbuch der Kristalloptik*, *Teubner*, 1906, 309, 328.
3. Bruhat .. *Traité de Polarimétrie*, 1930, 319.
4. Voigt .. *Ann. Physik*, 1902, **9**, 367.
5. Sommerfeld .. *Optics*, Academic Press Inc., 1954.
6. Born .. *Optik*, Springer, 1933, 414.
7. Ditchburn .. *Light*, Blackie & Son, 1952, 492.

APPENDIX

Since the index ellipsoid defined by the tensor (a), and the inverse gyration-vector Γ may be directly taken as the phenomenological quantities required to describe the propagation along any particular direction **s**, the relation between Γ and the gyration-vector **G** would not usually be required. The relation may however be obtained by writing (2) as $\mathbf{D}=\mathbf{D}' + i\mathbf{P}''$, where

$$\mathbf{D}' = (\epsilon)\,\mathbf{E};\ \mathbf{P}'' = \mathbf{G}\times\mathbf{E} \tag{11}$$

Substituting for **D** in (2 a)

$$c^2\mathbf{E} = (a)\,\mathbf{D}' + \Gamma\times\mathbf{P}'' + i\,(a)\mathbf{P}'' - i\Gamma\times\mathbf{D}'$$

Equating real parts and neglecting $\Gamma\times\mathbf{P}''$ in comparison with $c^2\mathbf{E}$:

$$(a) = c^2\,(\epsilon)^{-1} \tag{12}$$

Equating imaginary parts: $(a)\,\mathbf{P}'' = \Gamma\times\mathbf{D}'$. Choosing axes of co-ordinates X, Y, Z, along the principal electrical axes of the crystal, the X-component of this relation is

$$a_X P_X'' = \Gamma_Y D_Z' - \Gamma_Z D_Y'$$

or, by virtue of (11), if ϵ_X, ϵ_Y, ϵ_Z, be the principal dielectric constants,

$$a_X\,(G_Y E_Z - G_Z E_Y) = \Gamma_Y\,(\epsilon_Z E_Z) - \Gamma_Z\,(\epsilon_Y E_Y)$$

We may separately equate the coefficients of E_Y and E_Z occurring on both sides since this relation has to hold not just for *one* value of the ratio E_Y/E_Z, there being *two* polarised waves that can be propagated along the same direction. Hence, using (12),

$$\Gamma_Y = \frac{c^2}{\epsilon_Z\epsilon_X}\,G_Y;\ \Gamma_Z = \frac{c^2}{\epsilon_X\epsilon_Y}\cdot G_Z;\ \Gamma_X = \frac{c^2}{\epsilon_Y\epsilon_Z}\cdot G_X \tag{13}$$

The relation between the components of the modified gyration tensor and those of the gyration tensor may now be easily written down:

$$\gamma_{1i} = \frac{c^2}{\epsilon_Y\epsilon_Z}\,g_{1i};\ \gamma_{2i} = \frac{c^2}{\epsilon_Z\epsilon_X}\,g_{2i};\ \gamma_{3i} = \frac{c^2}{\epsilon_X\epsilon_Y}\,g_{3i} \qquad (i = 1, 2, 3).$$

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